Samir Kopačić, BSc

"Odor development of polymer coated cellulose-based materials"

MASTER'S THESIS

to achieve the university degree of

Diplom-Ingenieur

Master's degree programme: Chemical and Process Engineering

Submitted to

Graz University of Technology

Supervisor

Ao. Univ.-Prof. Dipl.-Ing. Dr.tech. Erich Leitner

Institute of Analytical Chemistry and Food Chemistry

Graz, March 2015

AFFIDAVIT

I declare that I have authored this thesis independently, that I have not used other than the declared sources/resources, and that I have explicitly indicated all material which has been quoted either literally or by content from the sources used. The text document uploaded to TUGRAZonline is identical to the present master‘s thesis dissertation.

Date	Signature

Abstract

The coated cupboard is a raw material used for either hot or cold drinks cup. These cups are coated by low density polyethylene in order to increase the barrier capacity of the cupboard. Furthermore, these cups must fulfill numerous regulations. These legal requirements cover substances of toxicological concern as well as substances which can induce any unwanted changes in the sensory properties of the product.

From the perspective of consumers, odor development is a major issue for this special food packaging. The aim of this work was to identify odor active compounds in raw materials and finished product and the potential sources of odor formation during the production of the compound material.

In the first part of this experimental work, pulp, polyethylene, uncoated and coated paperboard were investigated respectively to odor. The odor active compounds identified in these samples were aldehydes: hexanal, heptanal, octanal, decanal, nonenal and (e)-2-nonenal. Theoretically, other odor active compounds besides aldehydes could also be found in those samples. The second part of the experiments dealt with the analysis of the semi-finished products such as corona treated and corona untreated samples. The investigations were done by the one-dimensional and comprehensive gas chromatography coupled with mass spectroscopy as well as sensorial analysis. The extraction of the desired odor active compounds was done by the headspace solid phase microextraction.

Pulp and uncoated paperboard has lower odor activity values than coated paperboard and semi-finished product, such as coated paperboard without secondary corona treatment.

The same amount of corona applied on the material with different technical parameters such as grammage and coated polyethylene amount has different efficacy. Thermal treated low density polyethylene has a higher aroma active value at 215 °C than at 200 °C.

The clear correlation between off-odor raw materials and finished product is not possible because of the different quality of the raw materials. It can be stated however, that odor development is significantly influenced by the process parameter of the coating plant.

Acknowledgments

This thesis was a collaborative project between the Mondi Uncoated Fine Paper GmbH and the Institute for Analytical Chemistry and Food Chemistry of the Graz University of Technology. I would like to thank project leader DI Uwe Geistler and project supervisor Dr. Martin Messner. I appreciate the great opportunity they gave me to be part of this project, in addition to providing me with technical and financial support.

I owe many thanks to my supervisor Professor Erich Leitner for his excellent guidance, our many interesting discussions, and for giving me a lot of autonomy for this research. I want to thank the whole team in Professor Erich Leitner research group for providing daily support in the lab, especially to Dr. Barbara Sigmund for a great cooperative working relationship.

The invaluable education I have received at TU Graz was generously supported by the Mondi Austria Private Foundation. I gratefully thank the foundation's founder Dr. Veit Sorger and his co-workers for granting me this scholarship and enabling the fulfillment of this work. I want to also thank the Austrian Agency for International Mobility (OeAD), for supervising my academic progress, and for providing major support in different ways during my time at TU Graz.

Lastly, I must thank my parents, my grandparents, my sister, and my girlfriend for their unconditional support during these past years. Thank you for believing in me, for always having time for me, and for always giving me plenty of advice which helped me towards achieving my goals.

I would also like to take the opportunity to show gratitude to all of my friends for the great times we spent together at the university and for the friendly advice they gave to me these past years.

Graz, March 2015 Samir Kopačić

Table of Contents

List of Tables

List of Figure

1. Introduction

1.1 Problem with odor development

This thesis deals with the investigation of off-odor and odor development of paperboard for the cupboard production. Odor is very important property of the material and could be generated through different chemical processes. [38] Those chemical processes mostly result from raw material, but they can be intensified through manufacturing processes. Furthermore, there is a necessity to study every manufacturing step individually and to find the critical points of each process for better understanding of the odor development. There has been extensive scientific work done in the field of flavor or aroma chemistry, which helps to describe and understand the odor of materials in a chemical context. This problem is specific however, for one manufacturer of paperboard and because of that, should be handled in a specific way. That means studying the odor of a single material like pulp, paper or polyethylene does not give a sufficient answer for how the material comes to develop an odor and in which part of the manufacturing process mostly causes the odor development.

The fact that odor is generated from the raw materials, the raw materials are the main investigation topic. The best results could be reached just with the analyzing of process parameters and raw materials.

1.2 Paperboard in Packaging Industry [1]

The packaging industry is one of the most progressive industries in the world and food packaging is a major business sector. Today many paper manufacturers recognize these trends and switch from the conventional paper, like office paper, to the packaging segment. The food packaging system consist of food product and food packaging, which means that food producers as well as packaging producers are both challenged and strive to achieve the best, in order to satisfy the consumers and to ensure legal requirements. Food packaging has high standards of quality and safety to meet all requirements mandated by the governmental regulations in order to be placed on the market well.

Among many packaging materials which are used by the food producer, paper and paperboard play a very important role. Sometimes they are combined with others

materials like plastic for achieving the best packaging solutions. The selection of these materials is mostly determined by the properties and type of the food being packed. The technical, environmental, and costs issues of these combined materials should also be considered.

The paper and paperboard have been for a long time the key materials for food packaging. The difference between these two is that paper is lighter than paperboard and therefore has a different application.

The major advantage of the paper and paperboard packaging are low cost, machine processing ability, easy collection, biodegradability, and recycling, among others. The printability of the paperboard packaging is one of the most important attributes and opens free room for a lot of marketing. From the technical point of view, paperboard can be combined with other materials, such as polymers and metals. The main purpose of different material combination is a change in the barrier properties.

2. Paperboard

2.1 Paperboard as a Material

Paperboard consists of biogenic raw materials such as cellulose, hemicellulose, residual wood resins and lignin. [2] One small percentage of components of the paperboard are chemical additives, which have different functions and improve the physical, optical or strength properties.

Paperboard for food packaging could be produced either from recycled or virgin fibres, depending on the purpose the food packaging is used for. The mixtures of both are also very common. [1] Pulping and papermaking are two different production processes and they consist of many production units. The chemical pulp which is used for investigated paperboard is produced in different countries and from different wood. This work exclusively used paperboard from virgin pulp.

Paperboard should be fully free of odor, especially if its purpose is to have direct contact with food. Besides the natural compounds of the paperboard, the additives or interaction between the fiber and printing or coating could lead to formation of odorants and could be a source of odorants emission. [4] The volatile aldehydes which are well known for their rancid odor could be formed through auto-oxidation of short -chain fatty acids. Probably the first oxidation can start in the bleaching process which is one process unit in the pulping. For many years the oxidative chemicals such as hydro-peroxide and ozone replaced the traditional chlorine bleaching. [2, 35]

In the paper production process any changing of the process parameters could influence odor formation, especially if the mills close the water system and try to increase the utilization of the waste water. In that case microbiological activities are possible causes of the odor development. [2]

2.2 Chemical Composition of Paper

Paper in a modern time is made from the lignocellulosic fibrous material, called pulp. Pulp could be produced through chemical or mechanical separation of cellulosic fiber from wood. The usual wood arts for the chemical pulp are softwood trees such as spruce, pine,

fir, larch and hemlock, and hardwoods such as eucalyptus, aspen, and birch. The pulp could also be produced from recovered paper. [3]

Cellulosic fiber is mostly made of cellulose and hemicellulose, and both of these components are carbohydrates. Cellulose is a macromolecule and the basic unit of the cellulose is D-Glucose monosaccharide, which are bound to each other with a β-1, 4-glyosidic bond. Cellulose with its molecular formula $(C_6H_{10}O_5)_x$ is highly polymerized and the degree of polymerization could be between 280 and 2000. The degree of polymerization during papermaking is between 1000 and 1300, and varies because of the different wood, which is used for preparing the pulp. [3]

Hemicellulose is composed of hexose and pentose. There are branched and unbranched hemicelluloses that are mostly short-chain macromolecules compared to cellulose. They act as a sealant between the fiber and fiber wall.

The third natural component of wood fibers is lignin, which is a three-dimensional macromolecule. The lignin structure depends very much on the plant or wood it was extracted from. It is a complex polymer of aromatic alcohols known as monolinguals. Lignin is most commonly derived from wood, and is an integral part of the secondary cell walls of plants and some algae. As well as hemicellulose, the lignin is also very important for the stability of fiber. Due to its chemical structure and many methoxy functional groups, it hinders the swelling of the fiber and it is responsible for yellowing of the fiber as well. These facts indicate the lignin is mostly extracted from the pulp to one certain grade. The amount of the lignin residual in the fiber depends on the pulp process and future paper application. [3, 11]

Besides the natural components of the fiber and the paper, the paper also consists of chemical additives, which are essential for improving the physical, optical, chemical, and electrical properties of the paper. These chemical additives are primarily sizing agents, optical brightening agents, biocides, wet strength agents, mineral fillers, and also provide retention aid, among other examples. [37]

Table 2.1: Chemical composition of the wood pulp [1]

Material	Structure	Approximate weight %
Fibers		
Cellulose	Crystalline	45
Matrix		
Lignin	Amorphous	20
Hemicellulose	Semi-crystalline	20
Water	Dissolved in the matrix	10
Extractives	Dispersed in the Matrix	5

2.3 Food Packaging – General approach [3]

For a long time the packaging has been undervalued compared to the value of the packed good, but today in highly industrialized countries the importance of the qualitative packaging and its material are being greatly realized. The absence of high quality packaging in any modern industrial field would be seemingly inconceivable.

According to the European Union (EU) regulations 89/109/EWG, packaging is classified as an article of daily use. For the case that they come into contact with food, packaging is further classified as food packaging. The main purpose of this packaging is to ensure and maintain the quality of the packed food and to protect the packed food from any quality loss. The food packaging must also provide mechanical protection and structure stability. [3, 8]

The food packaging must resist environmental influences such as water and oxygen diffusion. This level of protection allows for the packed food to maintain its humidity, aroma, and flavor. The packaging must also resist against any climatic change and should be able to resist ionizing radiation if exposed. [8]

Protection is crucial in the food packaging industry, and because of that food packaging should be able to protect the food from any kind of physical, chemical and microbiological contamination. The packaging should possess enough space for advertisement and marketing as well.

The EU regulations also state that food packaging must be designed and manufactured in a way, that falsification, thievery, or any other manipulation of the costs from the producers is excluded. Not least should packaging be secure for children and adults, which handle it in everyday life.

2.4 Paper and Paperboard as a Food Packaging Material

Paper and paperboard are used as primary (direct contact with food), but also as secondary (no direct contact with the food) packaging materials. The difference between the two distinctions lies in their physical properties. Paper is defined as material with a basis weight below 224 g/m^2, while paperboard exceeds 224 g/m^2. When the primary packaging used is paperboard, it is often coated with different polymers in order to lower permeability of water, gases and organic vapour. Examples for these kinds of polymers are polyethylene, polypropylene, polystyrol and wax. The combination of the coated paperboard with metallic materials such as aluminum is also very common. One example of these materials, known as composite packaging, is food packaging for milk products.[1,3]

2.5 Quality Demand – Food Packaging Material

The quality standards for the paperboard food packaging are designed in correlation with the final application of the products. Different applications of paperboard products need different qualities. The odor of the products is an important quality parameter for determining its compatibility with the product and its final use. This is particularly relevant for products such as chocolate, tobacco, and many other flavored goods, where the odor of the packaging material is a major determinant of its applicability. [3, 5]

Food packaging using paperboard is a very complex system of different substances, which potentially could taint the food in different ways. Most notably, the migration or emission of the chemical substances from the environment and packaging into the packed goods must be considered. The migration of substances was not the subject of this work and is not further assessed in this thesis. [3]

Another major problem for the food packaging industry is the emission of odors from the packaging material. The food packaging must be free of any kind of odor. The odor of the

food packaging is considered a contaminant and in excess amounts could taint the food. The odor is perceived on an individual basis and could therefore be very subjective. [34] Preventing odor contamination in food is difficult because the odor of materials such as paperboard can be very low, but if the material is in a closed room the concentration of the odor active substances could reach higher levels leading to food tainting. The off-odor characteristics and its development in the paperboard food packaging can derive from the naturally contained substances in the raw material or from the substances which are formed during the production or converting process.[3, 5]

3. Odor and odor development

3.1 Paper odor and its origins

Odor is a physical property that can be seen as a mixture of different odor-active substances. Every single odor-active substance contributes to a certain degree to the off-odor character of the material. Odor developing compounds in paperboard materials originated from: [7]

- Degradation and autoxidation products of the biogenic materials.
- Degradation products from different chemical additives used in pulping, papermaking, and paper conversion processes.
- Odor through interactions between paper and printing inks.[5,6]
- Microbiological processes in water systems on the paper machine and pulp systems.

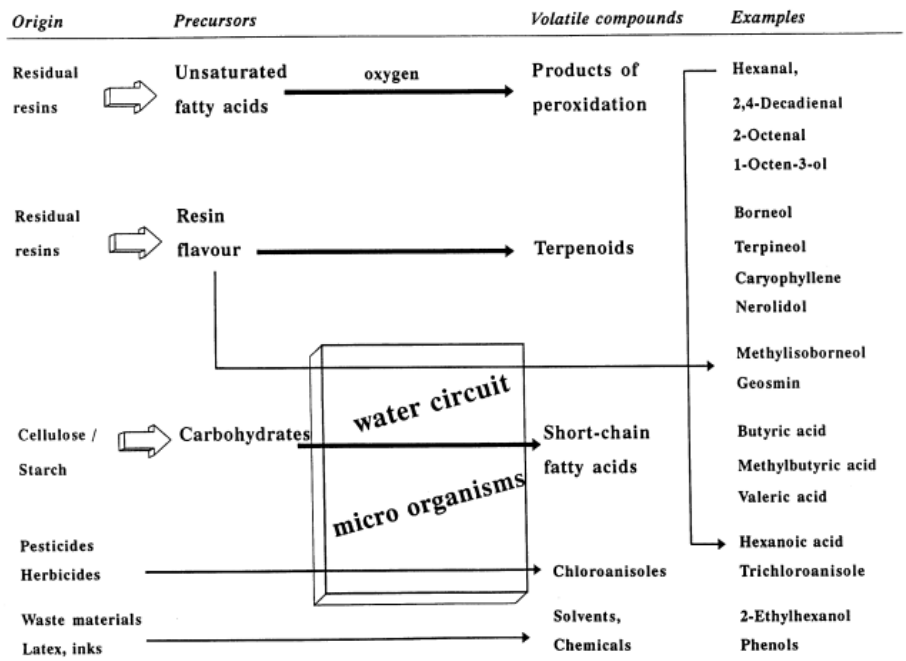


Figure 3.1: Natural Sources of odor and its development [2]

3.2 Raw Materials [8]

Wood, pulp, and paper composed naturally of hundreds different organic compounds, which are products of biosynthesis in the living organism. During the wood processing some of those compounds are chemically modified and decomposed. During the pulping of the wood, chemicals such as peroxide, oxygen and ozone are used to oxidize natural wood components. Many of the carbonic compounds formed are not odor active, but they act as precursors for the odor active substances.

There are more than 200 different volatile compounds (classified into eleven groups) which can arise through oxidation in the wood products. Some of these compounds are volatile, but not odor active.

- n-Alkanes (C2- C15)
- Branched alkanes (C4- C13)
- Alkenes (C2-C13)
- Aldehydes
- Acids
- Ketones
- Alcohols
- Esters
- Heterocyclic
- Aromatics
- Sulfur compounds
- Terpene

The precursors for many of those compounds are esters of higher fatty acids with glycerol and free fatty acids. The lipids in these natural woods are substrates for building the most prominent odor active substances such as aldehydes. The free unsaturated fatty acids are present both in hardwood and softwood. The amount of those is a bit higher in hardwood than softwood.

Around 20 different types of the fatty acids have been discovered in wood and processed wood products.

The acids involved in the lipid oxidation (the process creating the aldehyde) are oleic acid, linolenic acid, and linoleic acid. They are unsaturated fatty acids which could be very easily oxidized by the enzymes, photoxidation or autoxidation.

3.3 Aldehydes

This work establishes that the aldehydes are odor active substances which cause odor development and hence, their formation and properties must be analyzed. The six aldehydes with their respective sensory description and odor detection threshold are listed in the table.

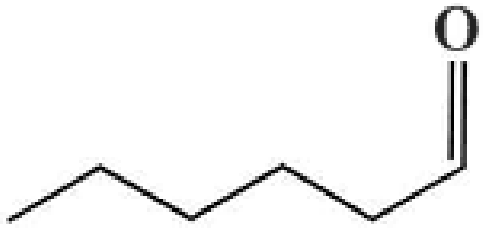


Figure 3.2: Chemical structure formula of hexanal [3]

Table 3.1: Sensory descriptions of various aldehydes [9]

Aldehyde	Sensory description	Odor detection threshold in Miglyol [µg/kg]
Hexanal	Green, grassy, fruity	75
Heptanal	Green, soapy, fatty, fresh, stink bug	28
Octanal	Citrusy, sweet, fruity, cardboard, metallic	21
Nonanal	Citrusy, sweet, soapy Moldy–cellar–earthy, cardboard, a bit fruity, dusty, old chair/house, fatty, goat stable	19
Decanal	Fatty, sweet, soapy, plastic, green, fruity orange, cleaning/washing detergent	21
(E)-2-Nonenal	Green, rancid, cucumber, stink bug, fatty	0.2

Aldehydes are light-weight acidic compounds due to their reactive carbonyl group. The products from the reduction and oxidation of aldehydes are alcohols and organic acids, respectively. [3]

The quantity of aldehydes formed during the oxidation of natural wood resins depends on the raw material. As already mentioned in the previous section, the main substrates are the unsaturated fatty acid, which appear in hardwood more frequently than softwood materials. The lipid oxidation can occur through autoxidation or photo-oxidation. The chemical mechanisms for this oxidation have been thoroughly examined in the field of food science. From one gram of oleic acid, linoleic acid, or linolenic acid, around 690 µg octanal and nonanal are produced. Linolenic acid is especially good for tracking the aldehyde formation, since hexanal appears in 5100 µg per gram linolenic acid and trans-2-octenal is found in 990 µg per gram linolenic acid. Hexanal has been examined in many scientific works as an indicator because of the high formation rate and abundance. [3] Figure 3.3 is a pathway of forming the volatile compounds, which cause odor. All reaction mechanisms described below lie under the same pathway, but vary under different conditions.

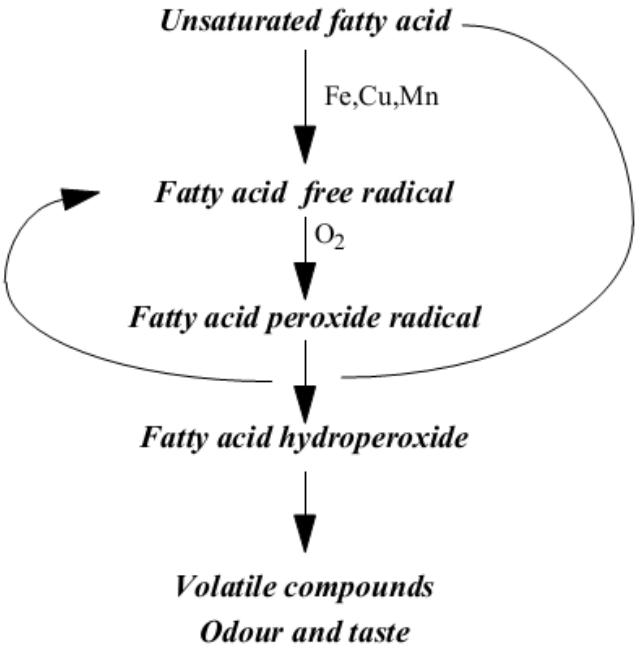


Figure 3.3: Chemical pathway of formation of volatile compounds [10]

3.4 Autoxidation

Autoxidation requires the presence of oxygen and is a characteristic oxidation process for many organic compounds such as ethers or unsaturated fatty acids. Much more of the unsaturated bonding in a fatty acid necessitates less energy to start the reaction. The metallic ions Fe, Cu, and Mn can catalyze and speed up the whole reaction, as one example. [11] These ions are very common in pulping, and usually they are removed by the complex molecule ethylenediaminetetraacetic acid (EDTA). [12] The autoxidation process can be separated into three steps and free radical reaction is determinant for the initial step. The first step removes energy (usually seen as photons) and at this phase there is a sign of no significant amount of oxygen intake. After some induction time and intake of oxygen the second reaction begins. In this phase there is no input of energy, but the amount of the oxygen needed for the reaction increases continuously. In the propagation state, the intake of oxygen is no longer needed. When once the hydroperoxide reaches the maximum concentration, they start to build the radicals and the chain reaction stops. [3, 11]

Figure 3.4 shows the detailed mechanism for the formation of hexanal from linolenic acid.

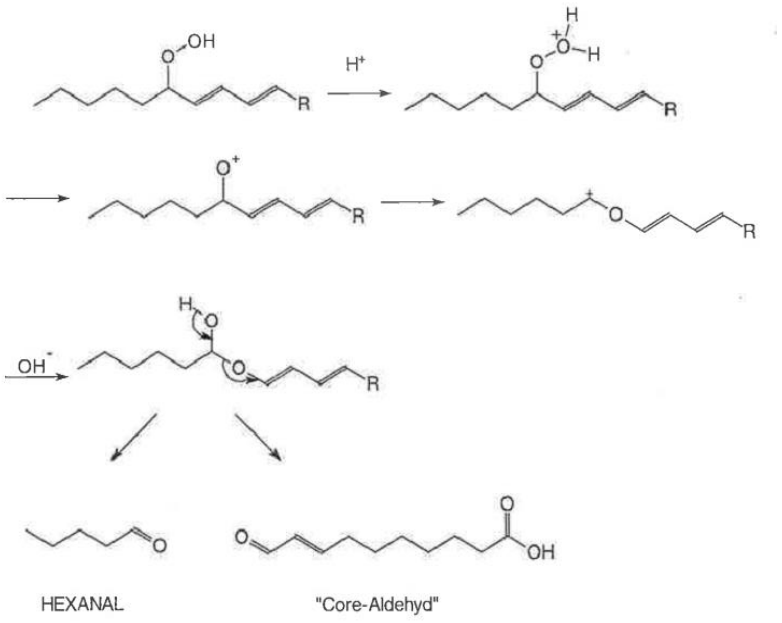


Figure 3.4: Hexanal Formation from the Linolenic Acid [11]

3.5 Photo-oxidation

The photo-oxidation, in a similar way as autoxidation, can cause the oxidation of the unsaturated fatty acid. The reaction necessitates the presence of light and oxygen to act as a carrier which can absorb light energy and transfer it to the double bond of the fatty acid. This kind of oxidation goes in two steps. The first step is formation of the hydroperoxide through the addition of the oxygen to the double bond. In the second step, the hydroperoxide is disrupted to the aldehydes. This reaction can be speed up in the same way as autoxidation through presence of metal ions like Fe, Cu and Co. Additionally, a surplus of light, high temperatures, and catalysts make the conditions for the reaction even more favorable. The hydroperoxide is odorless and does not contribute to the off-odor, but they remain unstable nonetheless. After their decomposition, the products are now volatile organic compounds like alkenes or saturated and unsaturated aldehydes, which cause the odors. [3, 11]

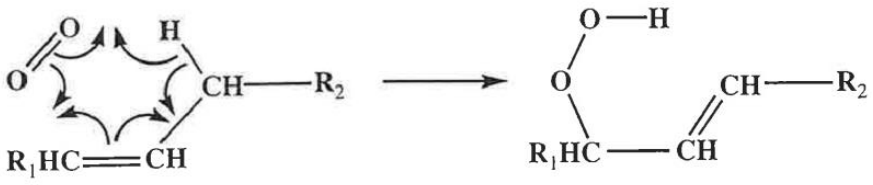


Figure 3.5: Mechanisms of cycloaddition of intake of oxygen by the double bond, and formation of peroxyl bond [3]

3.6 Enzymatic Degradation

The third method of lipid degradation occurs through two enzymes called lipoxygenase and lipase. High moisture content is a prerequisite for this kind of degradation, which was not the case in this work. The two enzymes operate as initiators of the oxidation reaction by attacking the double bond of the linolenic or linoleic acid, and remove the hydrogen radical. After the initiation step the process proceeds in the same way as autoxidation. [7]

4. Extrusion coating and coating material

4.1 Polyethylene

The extrusion process began 60 years ago with low density polymers being the most used in extrusion and until today, its application in extrusion coating was favorable. Polyethylene is a thermoplastic polymer and belongs to the polyolefin group. In extrusion it appears in a pellet form. Those LDPE pellets are mostly additive free, but occasionally may contain antioxidants, colorants, or slip additives. Besides the low density polyethylene (LDPE), there are also other grades like high density (HDPE), low linear density polyethylene (LLDPE), and so on. The difference between the polymers lies in their chemical structure and molecular weight distribution, which provides polymers with different physical and chemical properties. In the coating of the paper and paperboard LDPE acts as a moisture and gas barrier, providing favorable properties such as sealing, cleanness, transparency, and easy processing. LDPE is accepted by the paper and board convertors as a coating material for the liquid board, cupboard, and other food packaging. [13]

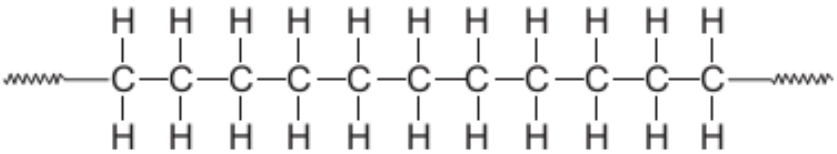


Figure 4.1: Polyethylene chemical structure [1]

4.2 Coating Extrusion

In the extrusion the polymer is being transferred from the solid to the melted state and mechanically pressed against the substrate. Pressure and the coating amount are adjustable in the extrusion die. In the figure below, the extrusion coating line for the paperboard is shown. It can be seen that the uncoated paperboard is pre-treated by the

corona in order to increase the hydrophilicity of the paperboard surface. For better adhesion between the hot plastic material and the paperboard, paperboard must be more hydrophilic. At the same time the plastic material is melted in the extrusion screw and through the extrusion die on to the paperboard surface. The coated paperboard is then cooled and corona treated once more. The second corona treatment increases the hydrophilicity of the applied polyethylene surface. The second corona treatment oxidase the polyethylene coated paperboard surface and improves the sealing ability. [32] In the cup-making process, adhesives are not used for many rational reasons and so the sealing ability of the polyethylene coated paperboard surface is crucial for the cupboard making process. The substrate could be coated on one or both sides, depending on the application of the coated paperboard. For example, coated cup boards are the main material for the drinking cups for hot or cold drinks. For hot drinks like coffee and tea, the cups are coated on one side with 8- 18 g/m^2. In order to avoid the condensation cold drinks cups are coated on both sides with 6- 18 g/m^2 plastic material in contrast to the hot drink cups. [13]

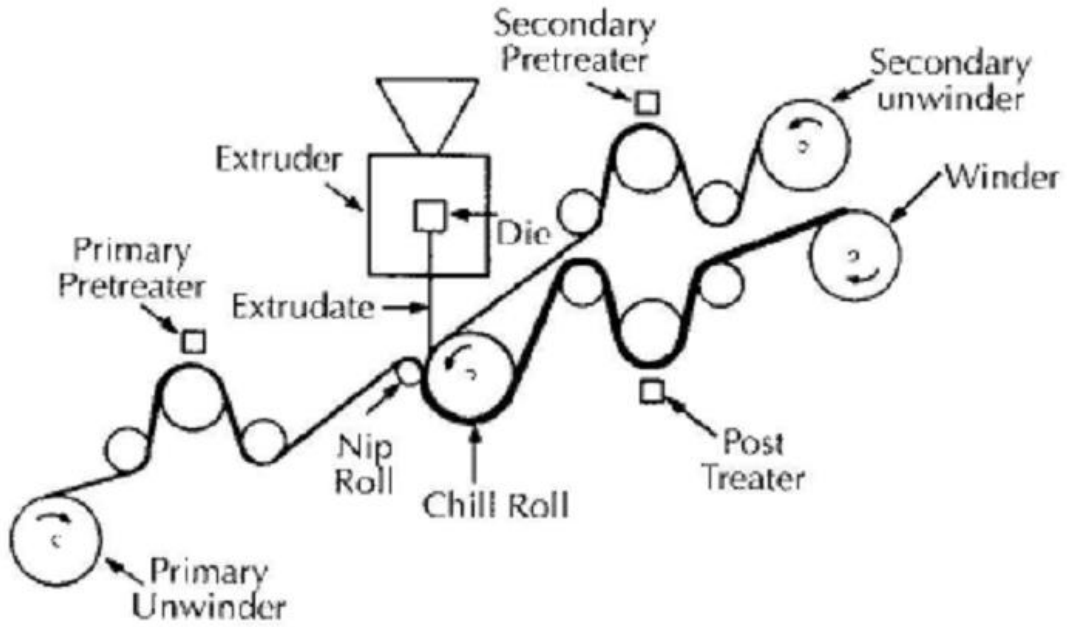


Figure 4.2: Extrusion coating plant with primary and secondary corona treatment [32]

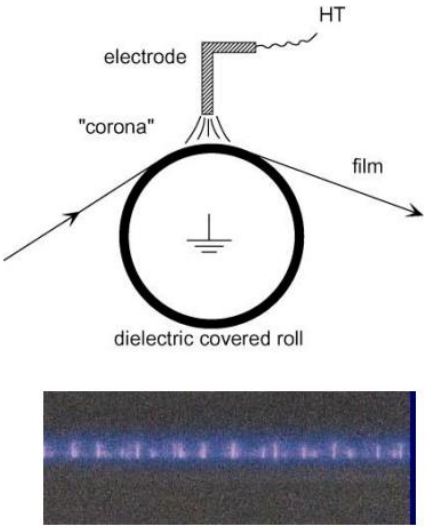


Figure 4.3: Primary and secondary corona treatment illustration on the extrusion plant [32]

The extrusion of paperboard is a continuous process, but from a technological point of view there are two significant unit operations. These are corona pretreatment (primary) and corona treatment (secondary), which is responsible for the oxidation of the paperboard surface and further oxidation of the LDPE coated paperboard surface. [32]

Extrusion coating processes are very demanding and if the best polymer grade is not used or if the process parameters are not in the optimal range, the odor problems could also arise by degradation of the low density polyethylene. [13]

4.3 Corona treatment

As already mentioned previously, corona treatment is needed to promote adhesion between the paperboard and polyethylene as well as to improve the sealing ability of the polyethylene coated paperboard. It is an electrical unit with a high frequency generator, high voltage transformer, and a treater station. The generator is control unit and it controls the desired amount of power, which should be applied on the load area. The power of the corona treatment could be expressed through the formula below. In this formula the main technical parameters are web width, line speed, and applied power. [13, 14]

*Corona dosage = generator power / (web speed * treatment width)*

$$D = \frac{P}{CB * v}$$

Equation 4.1: Corona [14]

- D- Corona dosage (W min/m^2)
- P- Generator power
- CB- Treatment width (m)
- v- Web speed (min/ m)

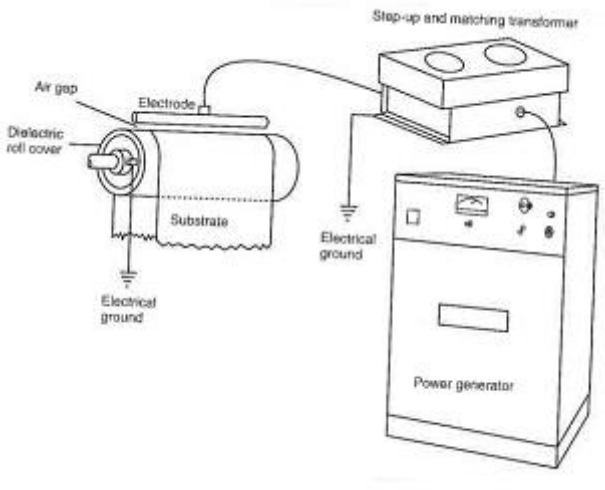


Figure 4.4: Corona station with the high voltage station [32]

In general the corona operates through applying the ionized gases on the substrate surface. By applying the high voltage and high frequency power on the air in the air gap, the ionized gas is formed. This starts the oxidation process on the substrate, which leads to the formation of many hydro peroxide, alcoholic, and carboxyl bonds and therefore increases the hydrophilicity of the surface. Oxidation of the air causes the formation of ozone, which can lead to further oxidation of the substrate surface. The ozonolysis reaction is well-known in organic chemistry because of reaction effectivity. Many industrial applications rely on this ozonolysis reaction, since ozone has excellent reactivity with polyolefin. [24]

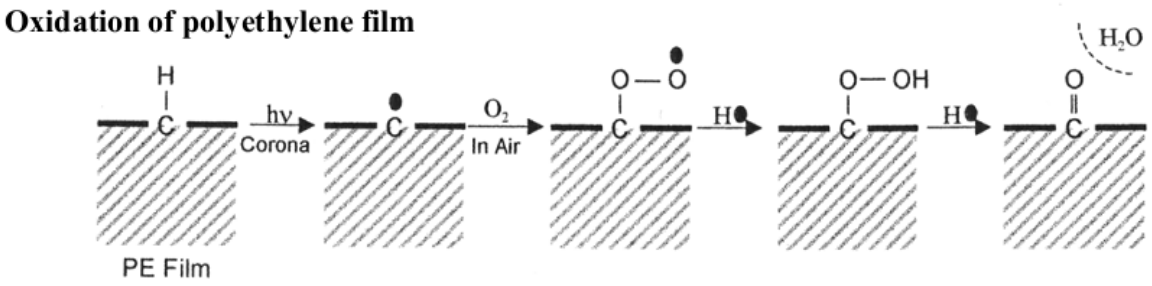


Figure 4.5: Oxidation of polyethylene surface [32]

4.4 Odor problems with polyethylene extrusion coating

Polyethylene as a material that readily undergoes oxidation processes, especially in the environment like coating extrusion, where the highly stimulating oxidation parameters like high temperature and ozone formation dominates. [26, 39]

The thermal oxidative degradation of polyethylene is chemically very similar to the degradation of the fatty acid. In the first step, alkyl radicals form and due to oxygen presence, the reaction goes further where the hydroperoxide is formed. As already mentioned in an earlier section, the hydroperoxide leads further to the formation of many organic volatile compounds such as ketones, alcohols, aldehydes, acids, and esters. [16, 17, 18]

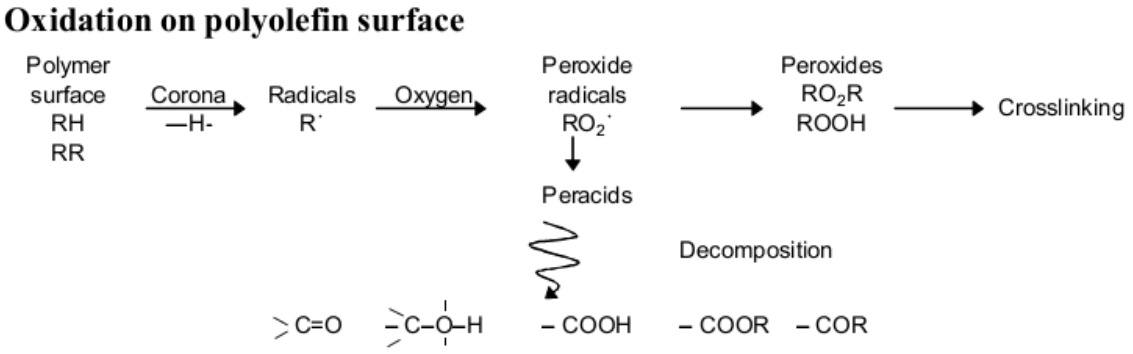


Figure 4.6: Oxidation of the polyolefin surface in the extrusion plant influenced by the corona and oxygen [32]

Table dominant odor active compounds at polyethylene oxidation are in the table 4.1. The table below shows the odor description of the common odor active aldehydes, which are formed from the polyolefin oxidation.

Table 4.1: Most common odor active compounds from the polyethylene oxidation [9]

Compound	Odor descriptors
Hexanal	Green, fatty
(E)-2-heptenal	Green, fatty, old, oil-rancid, stink, nuts
Heptanal	Green, soapy, fatty, fresh, stink bug
Octanal	Citrusy, sweet, fruity, cardboard, metallic
Decanal	Soapy, plastic, green, fruity
Nonanal	Citrusy, sweet, soapy Moldy–cellar–earthy, cardboard, a bit fruity, dusty, old chair/house,fatty, goat stable
(E)-2-octenal	Stink bug, green, fatty,
Δ-Octalactone	Coconut, sweet
(E)-2-decenal	Soapy, green, stink bug, pungent, rancid
2,3-Butandione	Butter, yogurt, sour cream
(E)-2-nonenal	Green, rancid, cucumber, stink bug, fatty
1-Octen-3-one	Mushroom, green, forest soil-earthy
1-Hexen-3-one	Plastic, unpleasant-pungant

Resulting from the thermomechanical stress and presence of oxygen, the first degradation product is already formed in the extrusion barrel. In the air gap, the melted polyethylene film is fully exposed to the oxygen atmosphere which accelerates the oxidation. After applying the polyethylene film to the substrate, the degradation proceeds further.

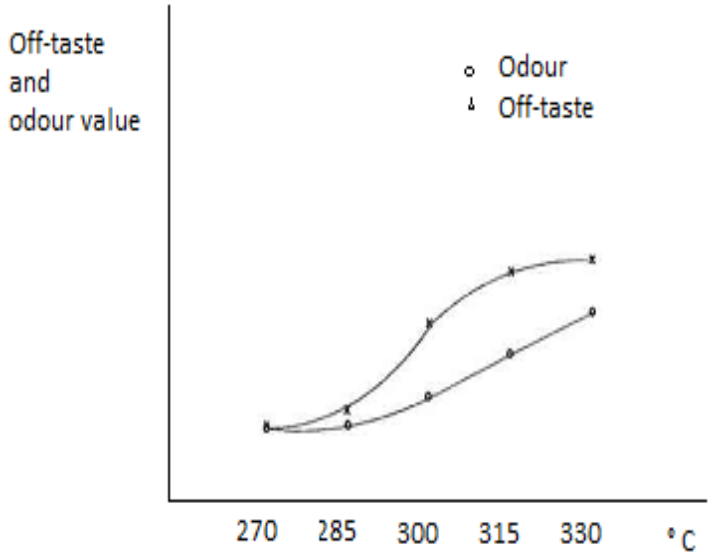


Figure 4.7: Odor and off-taste development in correlation with the temperature in the coating plant [13]

The formation of odor active compounds during the polyethylene extrusion depends on many factors, but the most usual which are described in the literature are:

- Extrusion temperature
- Film thickness
- Oxygen exposure
- Molecular weight distribution of the LDPE [26]

The extrusion temperature is crucial in the degradation of the polyethylene. The melting point of LDPE is around 110 °C and the extrusion temperature in many industrial coating plants reaches the maximum temperature at 325 °C. Many scientific works report the direct dependency between the temperature and the degradation of polyethylene and respectively, formation of the odor active compounds.

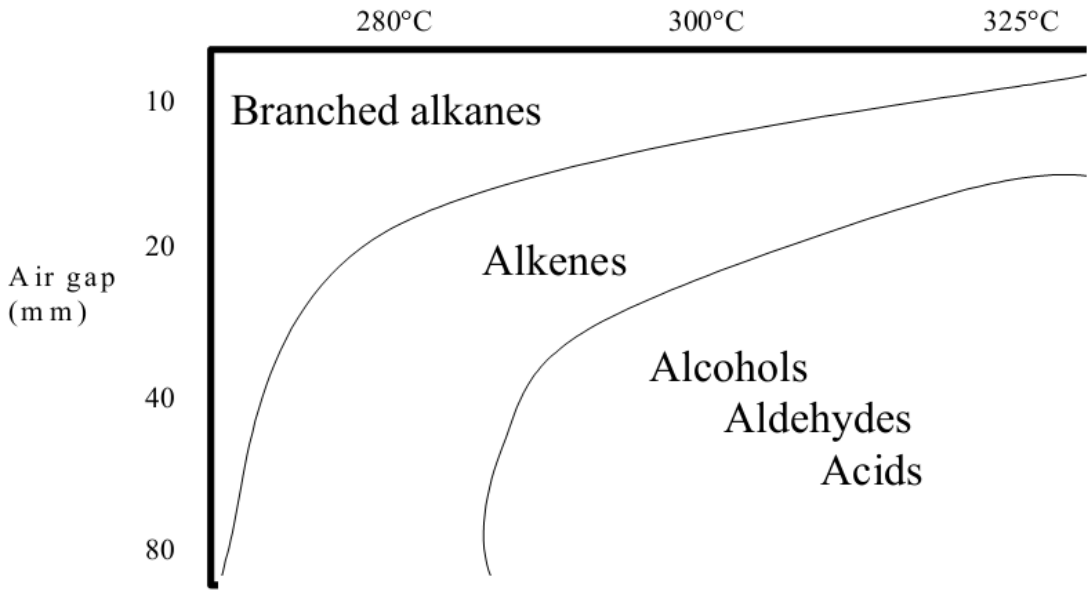


Figure 4.8: The influence of the air gap in the extrusion plant and melting temperature of the polyethylene is shown in the figure [39]

The thicker film generates more odor active compounds because of the slower cooling rate and its oxidation proceeds until it is quenched. The oxygen exposure is also one of the most important factors. In some plants the extrusion is done under an inert atmosphere in order to inhibit the oxidation. In the air gap the polyethylene melt is shocked and oxidized at a very high rate. This can be considered desirable because better sealing properties are acquired, however formation of aldehydes and acids are formed which cause the odors. [26, 39]

Molecular weight distribution may contribute to the greater presence of odors due to the fact that the polyethylene with a broad molecular weight distribution has more oligomers which decompose faster. [26]

5. Practical Part

5.1 Measurements Devices

The odor of the samples was investigated with instrumental devices, gas chromatography coupled with mass spectroscopy, and by sensory panel. These techniques are conventional methods for analyzing odor and in that manner were applied in this work.

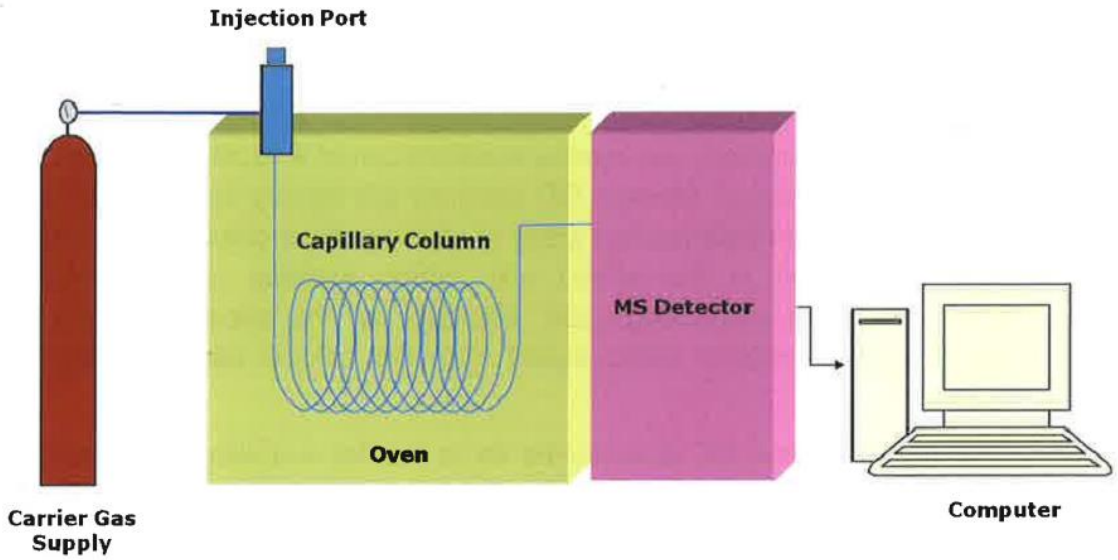


Figure 5.1: Gas chromatography coupled with mass spectroscopy [15]

5.2 Gas Chromatography - An Overview

Gas chromatography is a state of the art measurements device used to separate the components of the complex mixture of organic compounds. The prerequisite for the utilizing gas chromatography is the proper thermal stability of the organic compounds and the volatility. [15]

The analyzed compounds must be volatile in the range of 35 °C to 400 °C under absence of degradation or reactivity towards other compounds. The principle of gas chromatography is that the mixture of compounds is being vaporized in the injector port and then transferred on the column. Once on the column the mixture is separated and the analytes are identified by the appropriate detector. [23]

Gas chromatography instruments are very flexible devices and can be coupled with many types of detectors such as mass selective, flame ionization, electron capture detector, etc. The kind of coupled detector used depends on the analytical question.

Depending on the stationary phase, gas chromatography could be classified as either partition or adsorption chromatography. The basic units of a gas chromatographic system are:

- Carrier gas supply
- Injection port
- Column
- Oven
- Detector
- Data processing system [27]

5.2.1 Carrier gas

The carrier gas acts as a mobile phase and its role is to drive the volatile compounds through the column. It must be inert and chemically unreactive. In this work helium was used as the carrier gas. [27]

5.2.2 Injection port

Samples were introduced through the injection port into the column and depending on the volatility or the nature of the samples, there were many possibilities for the sample injection. Two conventional injector types are “on-column” (direct injection onto the column) and split/splitless (partial injection and evaporation in the liner). It is critically important that the injection port maintains consistent performance, reliability, preservation of sample contraction and efficient transfer to the column. [15]

5.2.3 Column

The interaction between the analytes and the stationary phase occurs in the column. The retention time of an analyte depends on factors such as the chemical structure of the analyte and its affinity to interact with stationary phase. The modern GC devices are equipped with open tubular capillary columns. The main advantage of this kind of column compared with the packed column is the higher speed of the material elution and better chromatographic efficiency. [27]

5.2.4 Oven

The column could be cooled or heated by changing the temperature of the oven. Temperature adjustments to the oven influence the separation efficiency. The partition coefficient of the analytes is influenced by the temperature and oven temperature provides further control thereby enabling good separation in the analysis. [23]

5.2.5 Detector

Chromatographic analysis of the volatile mixture does not afford any information about the chemical structure of the analyzed compounds. Some qualitative analysis is possible by using the retention time of the analytes, but this leads to incomplete information about the analyzed mixture. For that reason the GC is often coupled, especially in the field of flavor chemistry, with a mass selective detector.

Detectors in gas chromatography are units which are physically completely different from the rest of the instrument. For example, the mass selective detector works under vacuum conditions, while the gas chromatograph operates under high pressure conditions.

Mass selective detectors are coupled at the end of the column and ionize the separated analytes. The analytes are separated according to the mass: charge ratio (m/z). The parts of a mass selective detector are the ion source, the mass analyzer and the ion detector.

The molecule is ionized by the electro ionization and is fragmented. These ions or fragments are then separated by the mass analyzer according to their mass: charge ratio. The fragments are detected in the electron multiplier and the signals are generated. [27]

6. Sample preparation

6.1 Headspace Solid Phase Microextraction (HS-SPME)

In order to analyze the odor active compounds in biogenic material such as pulp or paperboard, the analytes must be extracted and isolated from the matrix and then introduced into the GC. In a complex matrix like paperboard, the volatile compounds are generated through several mechanisms. Compounds of interest may be:

- trapped in paper voids,
- dissolved in fiber and fines
- adsorbed onto fiber surface
- instantaneously formed through oxidation during the extraction

These releasing mechanisms of the odor active substances can occur separately as well as simultaneously. [20]

Headspace solid phase microextraction is a suitable method for the extraction, trapping, and isolation of the volatile odor active compounds. This sample preparation method and all of the release mechanisms stated above are covered by HS-SPME. [30]

This method operates in two steps and depends on two distribution equilibria. The first step is putting the solid or liquid sample into a vial and closing it. The vial is heated in order to activate some of the release mechanisms, whereupon some of the odor active substances are released from the matrix. The substances are accumulated above the sample and the first equilibrium is established between the sample and the gas phase above the sample. The selective extraction of the released substances in the headspace is done using coated fused silica fiber. The fiber is exposed in the headspace where it contacts the gas phase, allows for adsorption and absorption, and the second equilibrium is formed. The fiber with selectively extracted compounds is then introduced into the injection port and the substances are separated. [31, 32]

HS-SPME is seen as an accelerated method of sample preparation because of the facile handling, automation, high concentration ability, and because it does not require the use of a solvent.

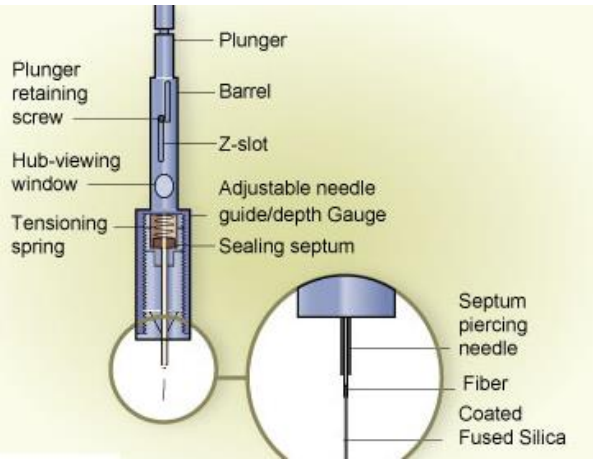


Figure 6.1: The solid phase microextraction with fiber [19]

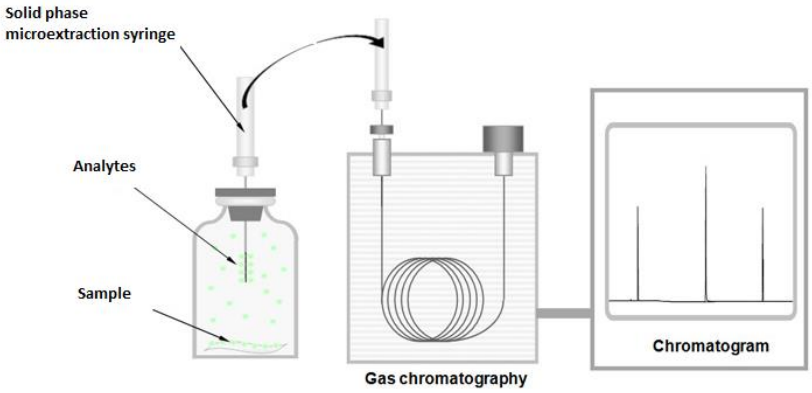


Figure 6.2: Gas chromatography with SPME [36]

6.2 Comprehensive Gas Chromatography

In order to precisely identify potential odorants in the samples, the multidimensional chromatography method used was comprehensive gas chromatography. Comprehensive chromatography is known as a “last destination” and is probably the most effective separation device today on the market. [22]

Analysis with comprehensive GCXGC provides multidimensional chromatograms and excellent screening.

Conventional comprehensive gas chromatography can be coupled with the same detectors as one-dimensional chromatography methods. The difference to the 1-D GC is

that comprehensive chromatography has two columns which are connected with a modulator. The second column is a short high speed high resolution column. Samples introduced into the first column samples are separated. The compounds go into the modulator where they undergo trapping, releasing, and focusing before being released into the second column. The resulting chromatograms are two dimensional with the retention time of the first column on the x-axis and the retention time of the second column on the y-axis. [23]

The comprehensive gas chromatography increases peak capacity, but requires very complex instrumentation, rapid detection system and customized data system.

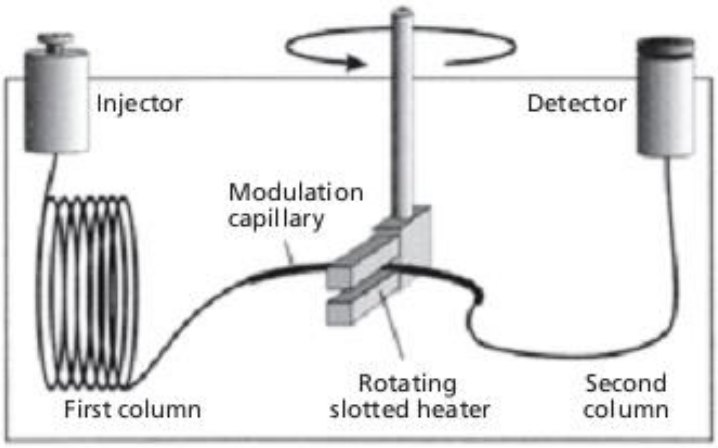


Figure 6.3: Comprehensive gas chromatography [22]

6.3 Sensory Analysis – An overview

Sensory analysis uses a group of either well-trained or untrained panelists able to test and evaluate the material or any other product respectively to odor. Through sensorial analysis, it is possible to recognize, describe, and obtain precise data of the flavor mixture of complexes. This method together with the instrumental analysis provides suitable results and is standard in every serious flavor analysis.

Humans have a very sensitive and discriminative sense of smell, which is triggered by the chemical stimuli. Normal adults can distinguish nearly 2000 different odor impressions, but a trained panelist can even discriminate from around 10000 different odor impressions. Odor perception takes place in the upper nasal activity, in the so called regio olfacotria. Odor active compounds must be volatilized in order to reach the regio olfacotoria. There are two ways for achieving that, the first pathway being transport with the breath air stream via the nasal cavity to the lounges. The second way occurs via the nasopharynx connecting the mouth with the nasal cavity.

Regio olfacotria is part of the nasal mucosal with an area of 10 cm^2 and it consists of around ten million receptors. Flavor sensation is cooperation between odor sensation and taste sensation. During eating, the taste of substances like sugar is registered in the mouth by the taste sensors and volatilized odor compounds reach the sensory olfactory region. Therefore, a flavor is defined as an overall sensation which includes the taste and odor sensations. The term “aroma” is often used as flavor, but according to literature the aroma in many countries is accepted as a pleasant odor. [34]

There are hedonic and analytic tests in the sensorial analysis. The hedonic test describes if something smells unpleasant or pleasant. It correlates consumer preferences and simulates until some point the consumer’s behavior perceiving the odor of the products. Untrained panelist and huge groups of people are desired to perform these kinds of tests. Analytical tests could be divided into two categories: descriptive and discriminative sensorial analysis, and are performed with experts that are highly trained panelists. The aim of the discriminative sensorial analysis is to investigate if there is a difference between the samples with respect to odor. The threshold sensitivity could also be a

subject of the investigation. The descriptive sensorial analysis is performed in order to describe the samples in the context of the human sensory. [28]

7. Description of the Samples

7.1 Samples

In order to understand which material contains more odor active compounds, raw materials (pulp), polyethylene, semi-finished and finished products had to be analyzed by GC. Chemical pulp is a raw material of uncoated paperboard and the pulp comprises around 95 % of the paper mass. The rest of the papers are chemical additives. The raw material for the finished product is uncoated paperboard. The finished product is polyethylene coated paper. For better understanding of the problem, semi-finished products of paper are also included and analyzed in the same way as all other samples.

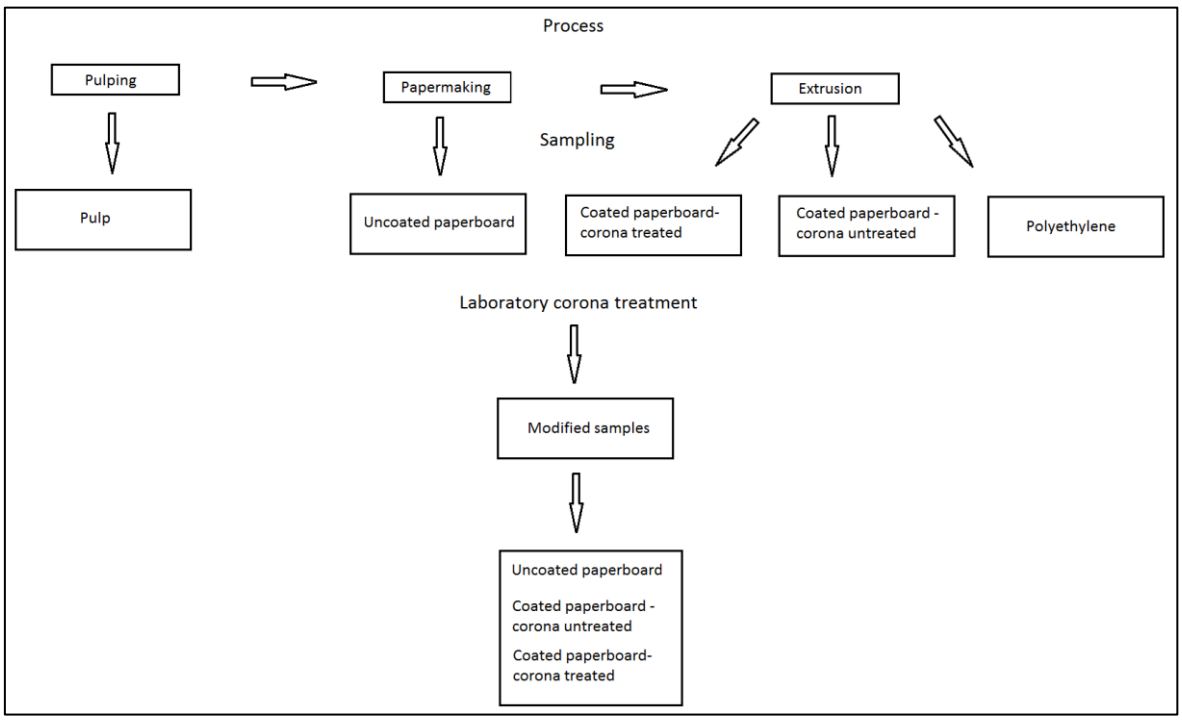


Figure 7.1: Sample drawing and modification

The figure 7.1 shows a sample drawing and the process of pulping, papermaking, and paper converting. The previous relations between the samples are also shown in this figure.

7.2 Pulp

The paperboard is produced from different kinds of chemical pulp and is the main raw material as well as the source of odor active compounds. Oxidation of natural wood components, which are also part of the pulp, leads to the formation of odor active compounds. According to the experience of papermakers, some pulp is more suitable for cupboard packaging than others. The idea of the analysis is to see if there is a difference between the different pulps respectively to odor.

The main aim of the pulp analysis is to see if the paperboard with high odor values correlates with pulp with high odor values. Secondly, the odor stability of the pulp should be investigated and a comparison between the pulp of the same art, but with a different production date, should be made.

Four different kinds of pulps have been analyzed for this purpose. The difference between the pulps was their production date, bleaching, and fiber length. The meaning of the sample name for one example is shown below.

Figure 7.2: Pulp (pieces 1x1 cm2)

Sample PA1

- *P- Pulp*
- *A- Letter designating sample name*
- *1-Sample number related to production date*

Table 7.1: Pulp samples

Samples			
Pulp	Production Date:	Bleaching:	Fiber length:
Sample PA1	16.07.2014	TCF	Short
Sample PA2	30.07.2014	TCF	Short
Sample PB1	12.06.2014	TCF	Long
Sample PB2	25.07.2014	TCF	Long
Sample PB3	01.09.2014	TCF	Long
Sample PC1	01.07.2014	ECF	Long
Sample PC2	15.05.2014	ECF	Long
Sample PC3	01.09.2014	ECF	Long
Sample PD1	28.07.2014	ECF	Short
Sample PD2	03.07.2014	ECF	Short
Sample PD3	05.09.2014	ECF	Short

The pulp could be bleached with chemicals like hydroperoxide, oxygen, and ozone in total chlorine free (TCF) process. The second bleaching process is the elementary chlorine free (ECF) process. Both of these processes are approved and standard in the pulp industry. [37]

7.3 Uncoated Paperboard

Uncoated paperboard is a material which is the finished product used by the paper convertors to make coated paperboard. Uncoated means that the paperboard has no polyethylene coating layer and is made solely from the pulp and chemical additives. The uncoated paperboard is always made out of the pulp mixture. Two or more pulps are mixed and one always has a shorter fiber and another longer fiber. The reasons for that have technological and economical implications. Considering that the paperboard is the source of active odor compounds, it has been analyzed in the same way as all other samples. Firstly, the idea was to see if any amount of the formed odor active compound was the same between the paperboard with the different parameters like grammage and used pulp. For the samples UB1- UB7, pulp which is known to be used by the manufacturer can be seen in the table 7.2. For production all other samples, used pulp is unknown and therefore the comparison between previously presented pulp samples could not be made.

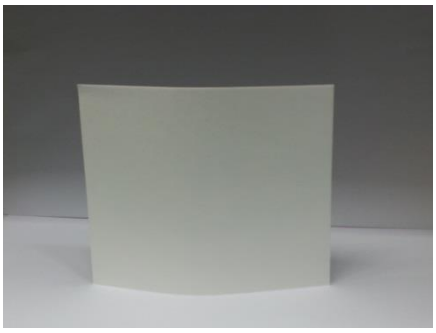


Figure 7.3: Uncoated paperboard

The table below lists uncoated paperboard samples and includes a description of their name with an expanded description given for one example.

Sample UB1

- *UB- Uncoated paperboard*
- *1-Sample number related to production*

Uncoated Carton Board

Table 7.2: Paperboard

Samples	
Uncoated Paperboard	Grammage [g/m^2]
Sample UB1	250
Sample UB2	210
Sample UB3	280
Sample UB4	300
Sample UB5	250
Sample UB6	280
Sample UB7	250
Sample UB8	280
Sample UB9	230
Sample UB10	40
Sample UB11	60
Sample UB12	50
Sample UB13	90

The first seven samples (UB1-UB7) are from the same paper manufacturer and are produced under the same conditions. The other samples were used as references and are supplied from different paper manufacturers. Samples UB10-UB13 from the table are not paperboard as indicated by the lower basis weight. The comparison between samples is still possible because of the fact that all of them should be odorless to some point and satisfy the customer's criteria for the odor.

7.4 Coated Paperboard

Coated paperboard is the finished product and it is used by the paper convertor for making the cupboard packaging. Previously discussed uncoated paper is used as a raw material for the coated paper. Uncoated paperboard is a carrier for a coating material (low density polyethylene). Coated paperboard has two sources of odor active compounds, polyethylene and paperboard. The finished products play the key role in this investigation and they were analyzed in the same way as all other samples. In the table below are coated paperboard and their technical parameters.

The aim of this analysis was to observe the difference between the coated and uncoated paperboard respective to odor. Many correlations were made between the raw materials and the finished products.

Sample CB1

- CB-Coated paperboard
- 1-Sample number related to production date

The sample CB1 is made of uncoated paperboard UB1 and therefore they have the same sample number. The naming system is consistent for all other samples.

Table 7.3: Coated paperboard

Samples		
Coated paperboard	Grammage [g/m^2]	LDPE [g/m^2]
Sample CB1	250	18
Sample CB2	210	18
Sample CB3	280	15
Sample CB4	300	15
Sample CB5	250	18
Sample CB6	280	18
Sample CB7	250	18
Sample CB8	280	18
Sample CB9	230	27
Sample CB10	40	10
Sample CB11	60	20
Sample CB12	50	15
Sample CB13	90	30

7.5 Semi-Finished Products

Semi-finished material could be classified into two categories: coated paperboard without the industrial corona treatment and corona treated material. These samples were partially produced in the laboratory and partially in the industrial process. The necessity for these kinds of samples was to investigate the odor formation, but also to see in which parts of the extrusion process lead to rapid formation of odor volatile compounds.

The reason for this analysis was to see the effect of the corona treatment, which is a part of the coating plant.

Name Description:

Sample CU1

- WC- Without corona- Industrial untreated corona samples
- CB- Coated paperboard
- 1-Sample number

Table 7.4: Industrial untreated corona samples

Samples		
Industrial untreated corona samples Coated Paperboard		
	Grammage[g/m^2]	LDPE [g/m^2]
Sample CU1	250	18
Sample CU2	210	18
Sample CU3	280	15
Sample CU4	300	15
Sample CU5	250	18
Sample CU6	280	18
Sample CU7	250	18

7.6 Laboratory Corona Treated Samples

Those samples are considered to be semi-finished materials and are modified in the laboratory with a miniature corona plant. Some of the samples with the numbers 1-9 are treated with corona and analyzed in the same way as all other samples. These samples can be classified into three further categories:

- Uncoated paperboard – treated with laboratory corona
- Industrial coated paperboard (corona untreated) - treated with laboratory corona
- Industrial coated paperboard (corona treated) - treated with laboratory corona

The samples were treated with the corona station at Montana University Leoben. Application of the lab corona device is a good simulation of the corona treatment in the coating plant.

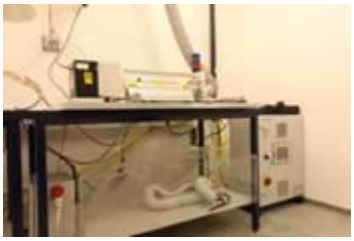


Figure 7.4: Laboratory Corona-Station (Ahlbrandt System) - Montana University Leoben

- Sample thickness up to 10 mm
- Generator power 100 – 800 W
- Surface oxidation via corona discharges

$$D = \frac{P}{CB * v}$$

Equation 7.1: Corona dosage [14]

- D- Corona dosage (W min/m^2)
- P- Generator power (W)
- CB- Treatment width (m)
- v- Web speed (m/min)

Example of calculation

Laboratory corona

- P- 400 W
- CB- 0,5 (m)
- v- 25 (m/ min)

$$D= 400\ W / (0,5\ m * 25\ m/min)$$

$$D= 32\ W\ min/m^2$$

7.6.1 Uncoated Paperboard

Sample name description:

Sample LCUB1

LC- With laboratory corona treatment

UB-Uncoated paperboard

1-Sample number

Table 7.5: Laboratory treated corona samples - uncoated paperboard

Samples	
Laboratory treated corona samples uncoated paperboard	
	Grammage [g/m^2]
Sample LCUB1	250
Sample LCUB2	210
Sample LCUB3	280
Sample LCUB4	300
Sample LCUB5	250
Sample LCUB6	280
Sample LCUB7	250

7.6.2 Coated Paperboard – Finished Product

Unfinished product is paperboard which is coated with polyethylene and treated with corona during the extrusion process. These samples have been taken and treated with corona in the laboratory.

Sample name description: *LCCB1*

LC- With laboratory corona treatment

CB-Coated paperboard

1-Sample Number

Table 7.6: Laboratory treated corona samples- coated paperboard

Samples		
Laboratory treated corona samples		
	Grammage [g/m^2]	LDPE [g/m^2]
Sample LCCB1	250	18
Sample LCCB2	210	18
Sample LCCB3	280	15
Sample LCCB4	300	15
Sample LCCB5	250	18
Sample LCCB6	280	18
Sample LCCB7	250	18

7.6.3 Coated paperboard- industrial corona untreated

Polyethylene coated paperboard which has not been treated with corona during the extrusion process was treated with the corona in the lab. The idea of this experiment was to simulate the industrial corona treatment and to observe whether the corona treatment has further influence on the odor development.

Sample LCCU

LC- Industrial corona untreated

CU- Coated and industrial untreated paperboard

1-Sample number

Table 7.7: Laboratory treated corona samples- coated and industrial untreated paperboard

Samples		
Laboratory treated corona samples		
	Grammage [g/m^2]	LDPE [g/m^2]
Sample LCCU1	250	18
Sample LCCU2	210	18
Sample LCCU3	280	15
Sample LCCU4	300	15
Sample LCCU5	250	18
Sample LCCU6	280	18
Sample LCCU7	250	18

7.8 Polyethylene Samples

Three different types of polyethylene granulates were analyzed. These three granulates were applied at the paperboard coating. The differences of the polyethylene are summarized in the table below.

Table 7.8: Polyethylene Granulate

Physical property	Unit	Granulate 1	Granulate 2	Granulate 3
Density	g/cm^3	0.918	0.920	0.915
Melt Flow Rate	g/10 min	7.5	7.5	15
Melting Temperature	°C	108	108	104

Figure 7.5: LDPE Granulate

8. Samples Preparation and Instrumental Parameters

All samples were prepared according to standard preparation procedures for analysis with SPME-GCMS. The samples were supplied commercially and in the form of A4-DIN sheets and were cut into squares (2x2 mm). Samples weighing 100 mg were put into 20-mL headspace vials and closed with an aluminum cap.

Polyethylene samples weighing 10-20 mg were prepared as opposed to the 100 mg mass of the other samples. The polyethylene samples were then thermally treated between 200 °C and 215 °C in the closed 20-mL vials and then cooled to room temperature.

For the quantitative analyses, 10 ng of the 3,3,5-trimethylhexanal internal standard was added per 100 mg of sample.

8.1 Extraction Method -Headspace- Solid phase microextraction

The samples were extracted with the automatized HS-SPME coupled with GC. Three different GC devices were used for this investigation and each one had a coupled headspace solid phase microextraction device. The fibers and coating material were consistent with each other in the three instruments (see the table 8.1-8.3). The extraction time was 20 minutes and the extraction temperature was 60 °C for the GCMS Agilent and GCMSD Shimadzu. Comparison of these two on the comprehensive GCMS identified 80 °C as a suitable temperature for the extraction. The experimental parameters for each analysis are shown in table 8.1.

Table 8.1: HS-SPME Methods coupled with GCMS Agilent

SPME Conditions for Agilent GCMS Analysis	
Fiber	SUPELCO 50/30 µm DVB/Carboxen/PDMS/Stableflex (2 cm)
Pre-Incubation Time	5 min
Incubation Temperature	60
Pre-Incubation Agitator Speed	250 rpm
Agitator On Time	5 s
Agitator Off Time	2 s
Vial Needle Penetration	20 mm
Vial Fiber Exposure	25 mm
Extraction Time	20 min
Desorption Temperature	270 °C
Desorption Time	10 min

Table 8.2: HS-SPME Method coupled with Shimadzu GCMSD

SPME Conditions for Shimadzu GCMSD Analysis	
Fiber	SUPELCO 50/30 µm DVB/Carboxen/PDMS,Stableflex(2cm)
Pre-Incubation Time	3 min
Incubation Temperature	60
Pre-Incubation Agitator Speed	500 rpm
Agitator On Time	5 s
Agitator Off Time	2 s
Vial Needle Penetration	20 mm
Vial Fiber Exposure	22 mm
Extraction Time	20 min
Desorption Temperature	270 °C
Desorption Time	10 min

8.2 GC-MS- Instruments Methods

Three different GCMS devices were used. The samples were separated on nonpolar and polar columns. The polar column was using with the GCMSD Shimadzu and the nonpolar column was used for the GCMS Agilent and for the GCMS Comprehensive. The experiments began with many qualitative analyses already completed in order to screen the sample and to get feedback about possible odorants. All quantification of the samples was performed on the GCMS- Agilent Technologies device. The experimental parameters are listed in the Tables 8.4. - 8.6 and the instruments were operated to ensure high experimental quality.

Table 8.2: Agilent GCMS Parameters

Instrumental Setting and Separation Columns	
Instrument	Agilent Technologies 5975C
Detection	Agilent Technologies VL MSD with Triple-Axis
	Column Parameters
Column	HP-5, 5% Phenyl Methyl -Siloxan
Column Length	30 m
Column Inner Diameter	250 µm
Column Film Thickness	0.25 µm
	Method
Method Parameters	
Carrier Gas	Helium/constant flow
Detection Temperature	280 °C
Injection Temperature	270 °C
Injector Mode	Splitless
Average velocity	32.76 cm/s
Total Flow	18.8 mL/min
Initial Temperature	-10 °C
Column Flow	2.4 mL/min
Oven Program	-10 °C for 1 min; 8 °C/min to 260 °C for 1 min
	Mass Spectroscopy
Ion Source Temperature	230 °C
Solvent Delay	7 min
Acquisition mode	Scan/SIM
Dwell time	30 s
Scan speed	1986 amu/s
Scan	44-300 m/z
SIM	44, 55, 57, 70, 83, 84, 98, 109 m/z

Table 8.3: Shimadzu GCMS Parameters

Instrumental Setting and Separation Columns	
Instrument	Shimadzu GCMS2010
Detection	MS-QP2010 Plus
Column Parameters	
Column	ZB-Wax plus
Column Length	20 m
Column Inner Diameter	180 µm
Column Film Thickness	0.18µm
Method	
Method Parameters	
Carrier Gas	Helium/constant flow
Injection Temperature	250 °C
Injector Mode	Splitless
Average velocity	46.2 cm/s
Total Flow	16.2 mL/min
Initial Temperature	35 °C
Column Flow	0.82 mL/min
Oven Program	35 °C for 1 min; 6 °C/min to 240 °C for 1 min
Mass Spectroscopy	
Ion Source Temperature	200 °C
Interface Temperature	280 °C
Solvent Delay	2.1 min
Acquisition mode	Scan/SIM
Event time	0.2 s
Scan speed	1428 amu/s
Scan	47-300 m/z
SIM	44, 55, 70, 83, 84, 98 m/z

8.3 Sensory Analysis– Method

The sensorial analysis was done according to the ÖNORM EN 1230-1- Part 1. The panelists were trained according to the DIN 10959. For the panel calibration, premium quality office paper was used. The analysis was done “blind”, where panelists were not given information related to the samples. The panelists were also experienced with analyzing packaging material. The samples were prepared and analyzed in the human sensory labor under standard conditions. Every panelist was given one sheet A4 (210 × 297 mm) DIN format. The sheet was cut into stripes 20 x 297 mm and placed into 500-mL screw top jars. The screw top jar was previously washed and baked at 100 °C. The samples were conditioned under room temperate for 24 hours before the sensorial analysis. Every panelist had one sample and one reference sample (a blank sample) and analyzed randomly.

The panelist marked the odor of the sample according to the odor grading system (from ÖNORM):

- 0 - absent
- 1 - barely perceptible
- 2 - medium
- 3 – intense
- 4 – very strong

If the sample had a medium odor (grade 2) or higher, the panelist gave an odor description of the sample. Each panelist analyzed five samples per day and a total of 22 samples were analyzed. The grade for the sample was given as a median of the overall panel grade. [33]

8.4 Qualitative and Quantitative Analysis

The qualitative analysis was performed with all three GC devices and chromatograms were analyzed to identify potential odor active compounds. The six aldehydes listed in the table 8.7 are odor active compounds analyzed for all samples. These odorants were present in raw materials, finished products, and modified products.

Table 8.4: Odor active analytes

Aldehyde	**Sensory description**	Odor detection threshold in Miglyol [µg/kg]	Reference Ion (m/z)
Hexanal	Green, grassy, fruity	75	44,55
Heptanal	Green, soapy, fatty, fresh, stink bug	28	44,55
Octanal	Citrusy, sweet, fruity, cardboard, metallic	21	44,55
Nonanal	Citrusy, sweet, soapy Moldy–cellar–earthy, cardboard, a bit fruity, dusty, old chair/house, fatty, goat stable	19	44,55
Decanal	Fatty, sweet, soapy, plastic, green, fruity orange, cleaning/washing detergent	21	44,55
(E)-2-Nonenal	Green, rancid, cucumber, stink bug, fatty	0.2	55,70,83

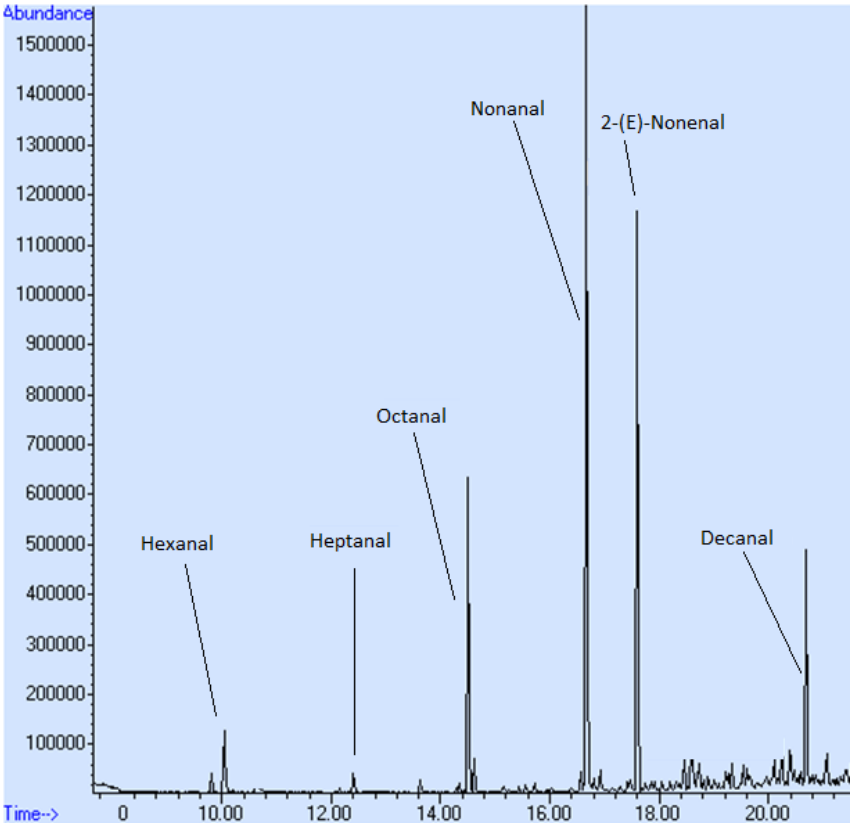


Figure 8.1: Coating paperboard –TIC Screening Agilent GC-MS

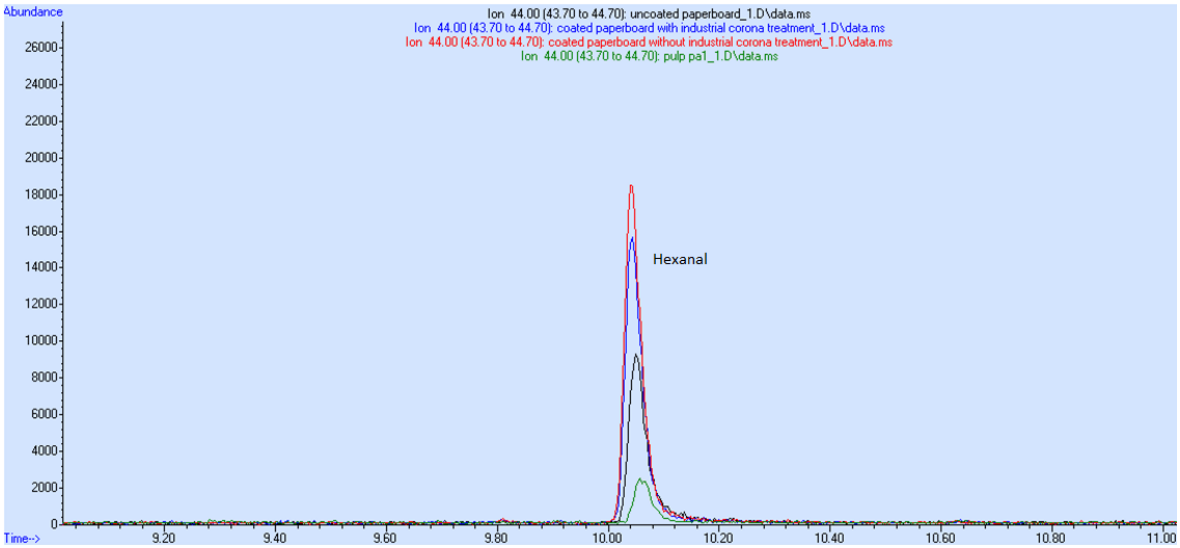


Figure 8.2: Hexanal molecule ion is extracted and peak area is compared between pulp, uncoated paperboard and coated paperboard- Agilent GC-MS

8.5 Standard Addition, Internal Standard, and Response Factor

The quantification of the analytes was done by standard addition. The aldehyde mixture with unsaturated and saturated analytes (C6- C10) was used in the quantification of the analytes. Standard additions were performed to determine which concentration range the analytes resided.

A more practical method for quantifying the analytes is by using an internal standard. The internal standard used for this quantification was 3, 3, 5-trimethylhexanal.

The first step which was to find the concentration range of each analyte and where the linearity was present. The response factor took into account the difference in the detector response between analyte and standard.

$$R_{x/IS} = (A_x / A_{IS}) / (c_x / c_{is})$$

Equation 8.1: Response factor (RF) [29]

- A_x- Peak area analyte
- A_{IS-} Peak area interne standard
- c_x- Concentration analyte
- c_{is}-Concentration interne standard

Table 8.5: Aldehyde mixture used for standard addition

Aldehyde mixture – C_6-C_{10}	
Unsaturated	**Saturated**
Hexanal	2-(e)-Hexenal
Heptanal	2-(e)-Heptenal
Octanal	2-(e)-Octenal
Nonanal	2-(e)-Nonenal
Decanal	2-(e)-Decenal

Table 8.6: Analytes with response factors and odor threshold

Analytes	RF	Odor detection threshold in Miglyol [µg/kg]
Hexanal	1.100	75
Heptanal	0.447	28
Octanal	0.482	21
Nonanal	0.976	19
Decanal	2.529	21
(E)-2-nonenal	1.326	0.2

8.5.1 Odor active value (OAV)

Some odorants contribute more to the overall smell of the sample than others. The odor active value, sometimes called the aroma value or flavor, indicates how much one odorant contributes to the overall scent.

"The OAV is defined as the ratio of the concentration of a single compound to the odor threshold for that compound" [34]

"Odor threshold is the minimum concentration of a substance at which a majority of test subjects can detect and identify the characteristic odor of a substance. While odor thresholds can serve as useful warning properties, they must be used cautiously because olfactory perception varies among individuals" [42]

8.5.2 Data Presentation

According to literature one of the best ways to present data is to summarize the odor activities values of each odorant, and present it as an overall odor activity value. The odor activity values had been calculated by using the formula 8.2. The OAVs of each analyte in one sample are summarized and presented as a sum or overall odor activity value.

ΣOAV_{Sum} (Odor activity value) = $OAV_{hexanal}+OAV_{heptanal}+OAV_{octanal}+OAV_{nonanal}+OAV_{2\text{-}(e)\text{-}nonenal}$

Equation 8.2: Overall odor activity value of one sample [42]

ΣOAV_{Sum} = 6.6+1+0.8+18.0+3.5+261= 291 - Sample CB1

A better comparison between the different samples (such as pulp or paper) could be compared respectively to different production dates or technical parameters.

In the table 8.9.1 below the concentration and odor description of the 2- (e) - Nonenal were compared. It is apparent that concentration has direct influence on the odor quality of the odor active substance.

Table 8.7: Odor quality of the 2-(E)-Nonenal in correlation with concentration [40]

2-(E)- Nonenal - Odor quality	
Odor description	**Concentration in Water [µg/kg]**
Plastic	0.2
Woody	0.4-2
Fatty	8-16
Unpleasant oily	30-40
Cucumber	1000

9. Results and Discussion

9.1 Results – Pulp

In this work is data presented from the pulp of four different pulp producers. Two or more pulp samples were taken from each producer and tested to see if the overall OAV is stable or varying. The lowest overall OAV for the pulp sample was 9 and the highest was 36. The figure 9.1 shows the distribution of analytes or odorants in one of the pulp samples. Furthermore, it can be seen how the amount of the odorants is not a determinant for the odor activity value. Although the hexanal has an average ten times greater amount than nonanal or 2-(e)-nonenal, the odor activity value of the last two analytes have much more influence on the odor of the sample. As previously discussed, hexanal is present in the highest amount where it is readily formed through the oxidation process of the linolenic acid and linoleic acid, and is seen as representative of all odorants.

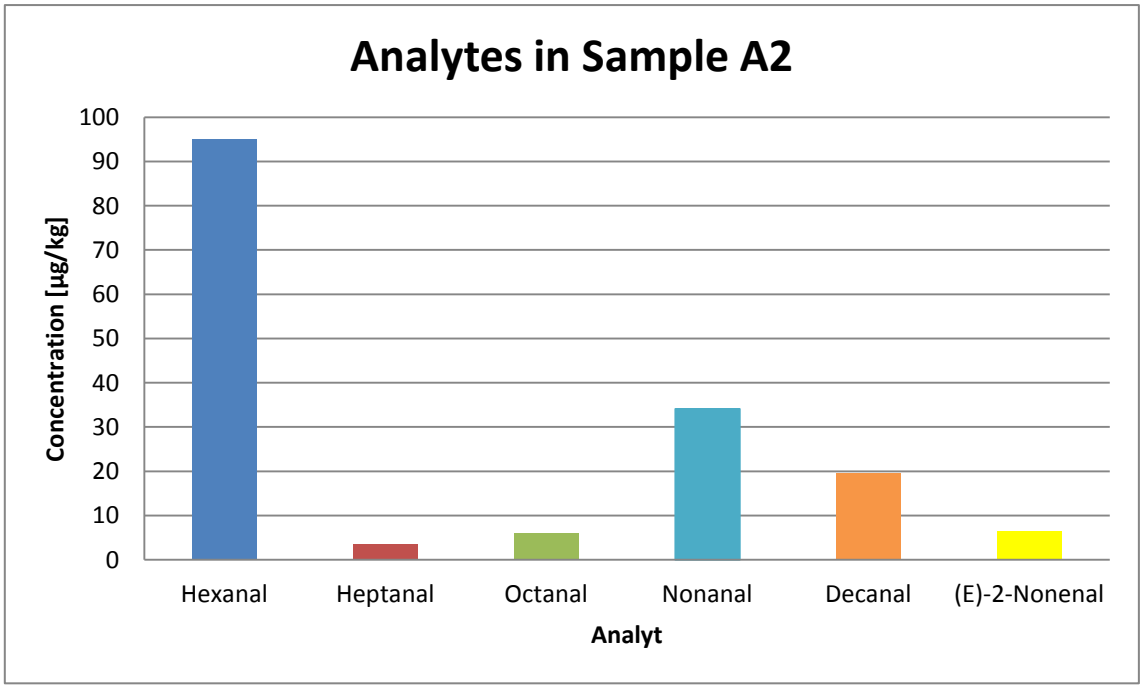


Figure 9.1: Odor active substances in pulp sample A2

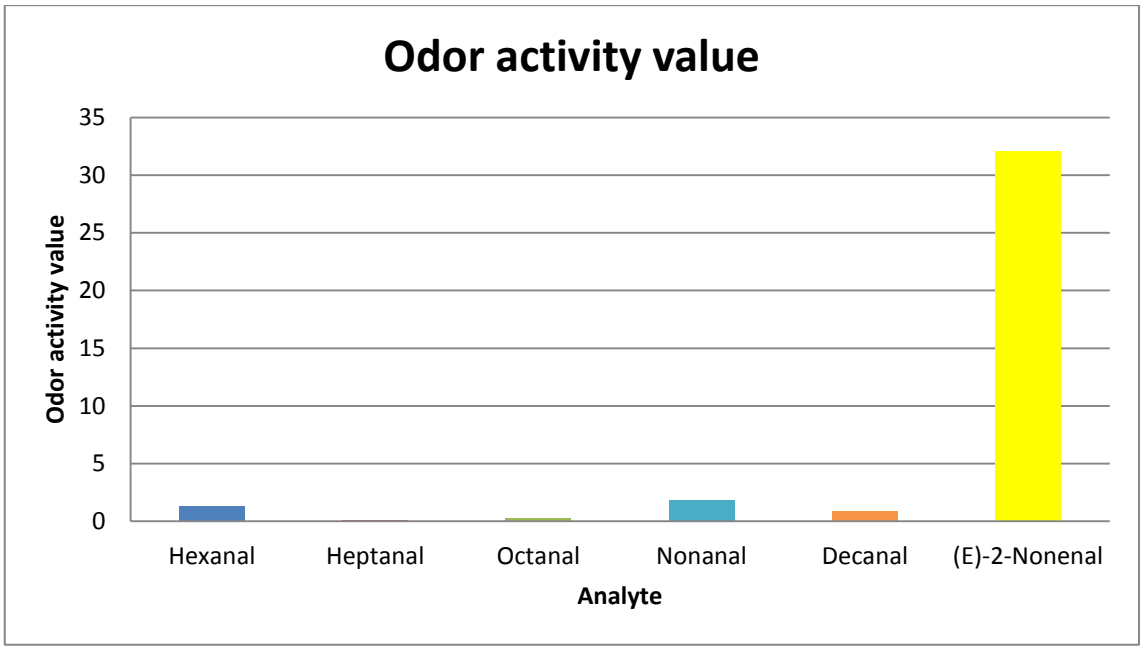


Figure 9.2: Odor activity values of the pulp analytes in sample A2

9.2 Sample Pulp A

Sample A is an example of the pulp analysis and can help explain the problem of the pulp results.

From Sample A, two different samples respective to different production dates are analyzed and the overall OAV for the sample A1 is 36 and for the sample A2 is 14. Pulp A1 and A2 are produced in Austria from the same wood or wood mixture and should have the same quality respectively to odor. These results are seen as big issues for the paperboard producers because of the varying odorant amounts in the samples.

Table 9.1: Odorants concentration and OAVs of sample pulp A2

Sample PA1		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	94.9	1.3
Heptanal	3.6	0.1
Octanal	6.0	0.3
Nonanal	34.1	1.8
Decanal	19.5	0.9
(E)-2-Nonenal	6.4	32.1
∑ OAV		36

Table 9.2: Odorants concentration and OAVs of sample pulp A2

Sample PA2		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	110.1	1.5
Heptanal	2.3	0.1
Octanal	2.9	0.1
Nonanal	10.8	0.6
Decanal	12.2	0.6
(E)-2-Nonenal	2.2	11.0
∑ OAV		14

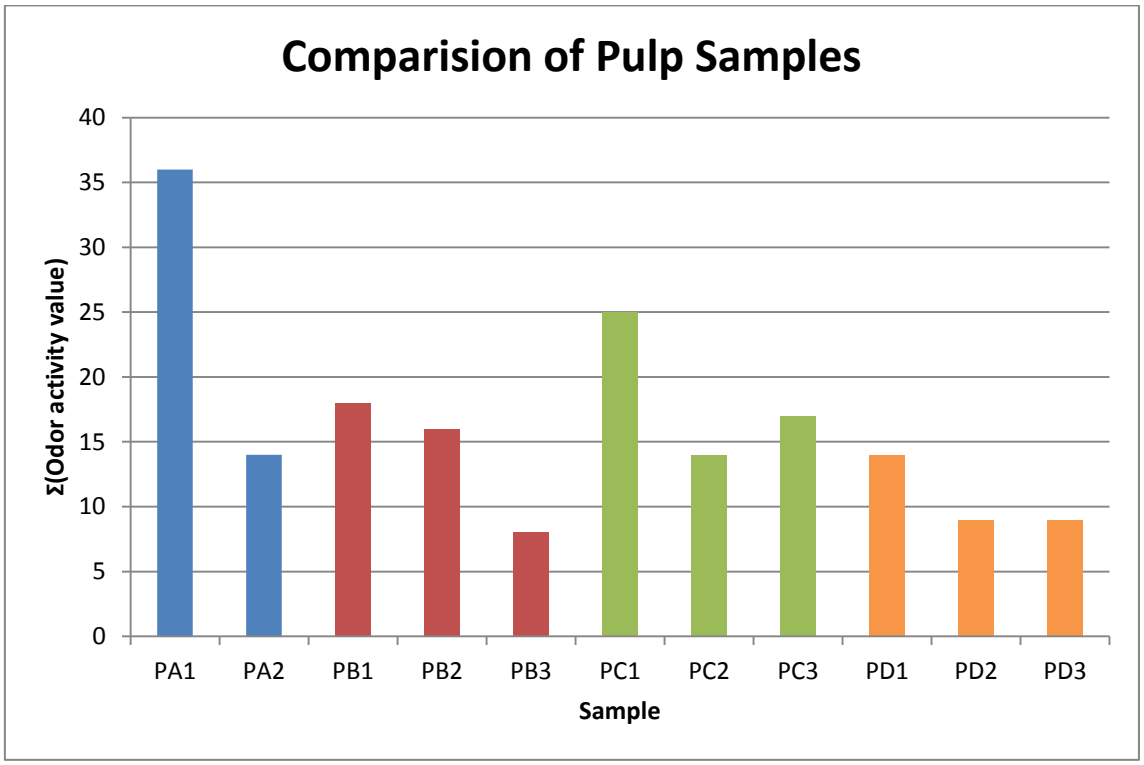


Figure 9.3: Comparison of the different pulp samples respectively to overall odor activity value

A repetitive trend can be seen from the figure which is typical for all samples included in this work. The first conclusion which can be derived from these results is that pulp quality respective to odor development differs from the different pulp supplier. Secondly, it can be concluded that the producers do not maintain the same quality of the pulp over time.

9.3 Results - uncoated paperboard

In total, data from 13 different uncoated and coated paperboard samples was collected for this work. The samples varied in terms of technical parameters and production dates. The lowest overall OAV was 19 for sample UB5 and the highest was 174 for sample UB6.

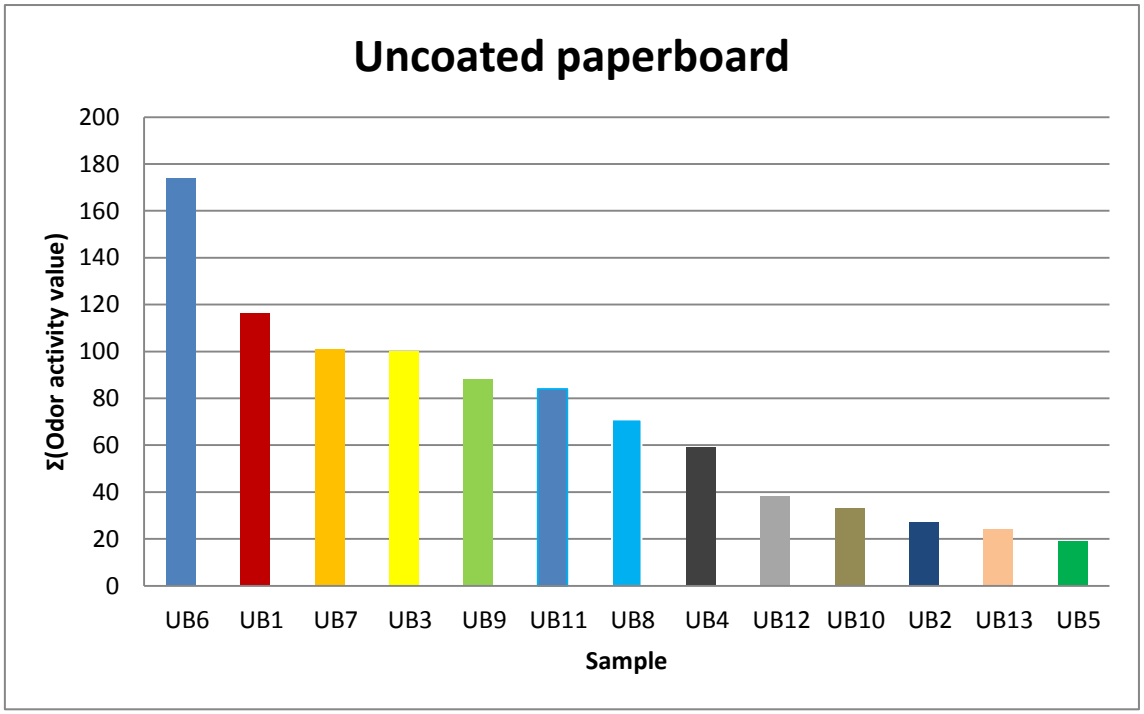


Figure 9.4: Comparison of the different uncoated paperboard respectively to overall odor activity value

The coated paperboard has a higher overall odor activity value than uncoated paperboard, and these are the first indicators of the contribution of the polyethylene to the odor development. The highest OAV was 493 for sample CB10 and the lowest was 101 for sample CB7.

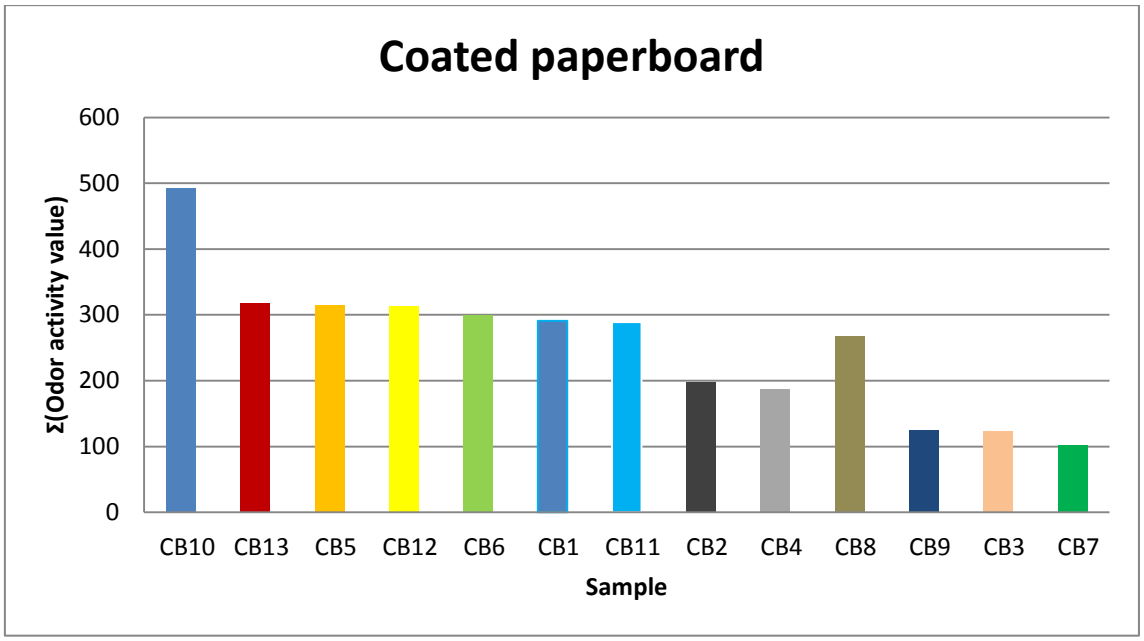


Figure 9.5: A comparison of the coated paperboard samples

9.4 Results – polyethylene coated paperboard- corona untreated

The samples designated 1-7 that were untreated with the secondary corona in the extrusion process are presented here. Notably, they are all acquired from the same producer and convertor. The lowest odor activity value was 209 for sample CU2 and the highest value was 462 for sample CU5.

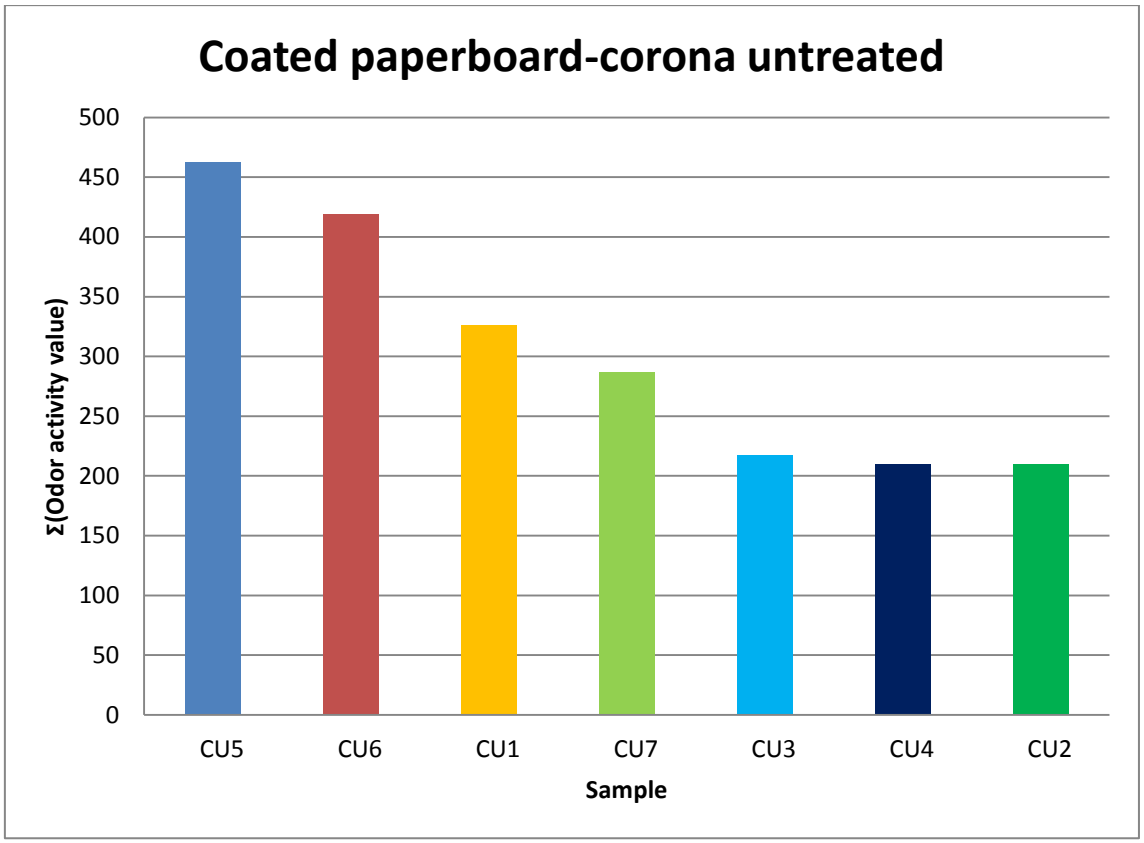


Figure 9.6: A comparison coated paperboard samples which are not treated by the secondary corona in the extrusion process

9.5 Results comparison – uncoated (UB), polyethylene coated paperboard-corona treated (CB) and polyethylene coated paperboard-corona untreated (CU)

On the figure 9.7 another trend was noticed. The uncoated paperboard has a lower value than coated paperboard, and the reason for that is that coated paperboard has two sources of the odor substances compared to the uncoated paperboard. These results confirmed the conclusion that polyethylene is a significant source of the odor active compounds. On average, the uncoated paperboard has 61.5 % smaller odor activity value than coated paperboard.

The second trend is that the coated paperboard finished product has on average a 20% smaller odor activity value than coated paperboard without secondary corona treatment.

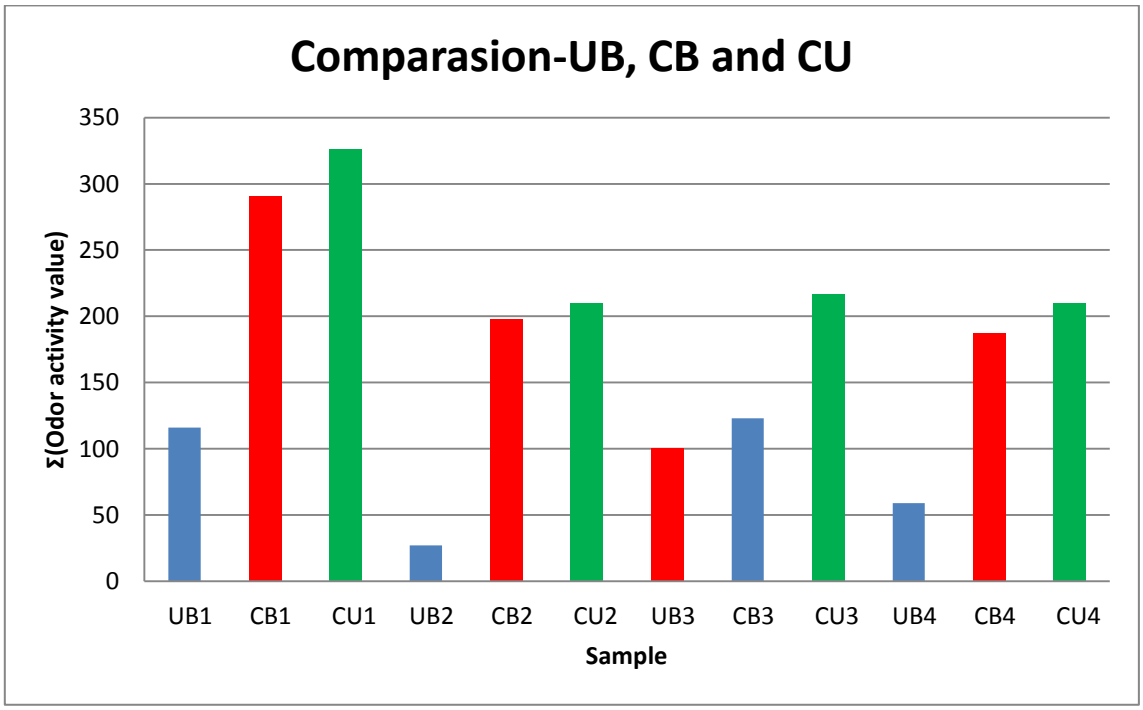


Figure 9.7: Comparison of overall odor activity value between uncoated (UB), coated paperboard (CB) and coated paperboard-corona untreated (CU)

10. Case studies: Results – Semi finished product

10.1 Uncoated paperboard-corona treated

On average, odor activity values of uncoated paperboard were higher after primary corona treatment. The higher oxidation rates driven by the corona could be responsible for this phenomenon.

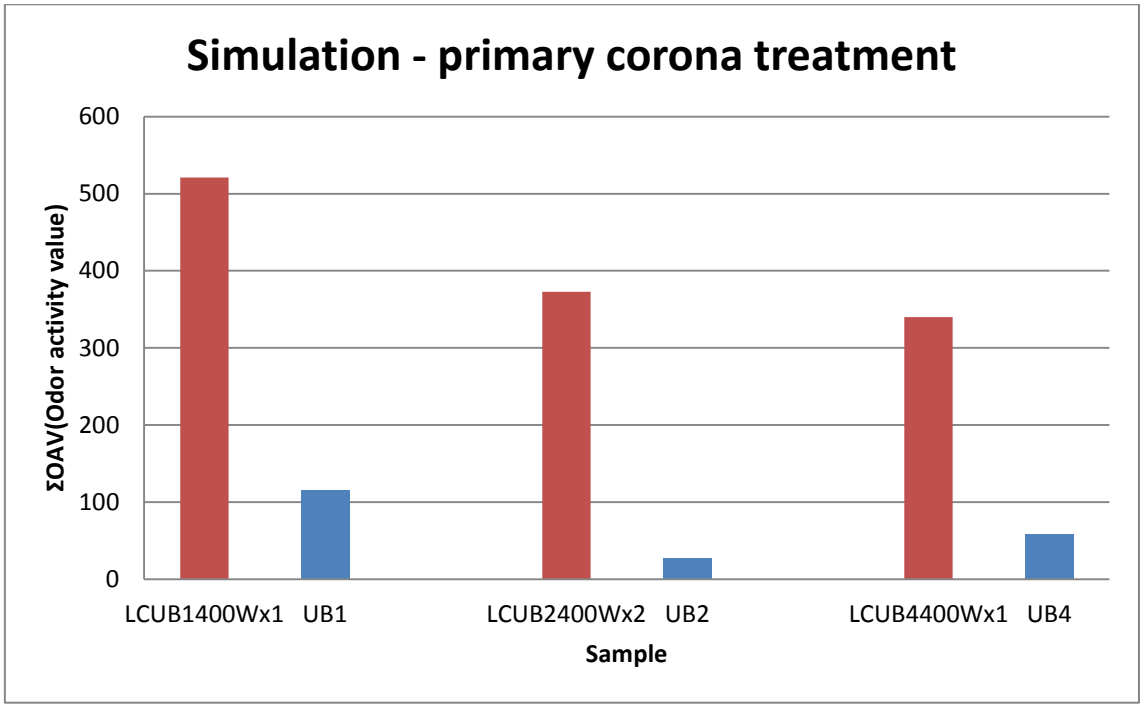


Figure 10.1: Simulation of primary corona treatment

Simulation of the secondary corona treatment in the laboratory showed that the odor activity values increases. The sample CU3 is treated by corona-power of 600 Watt two times and the sample CU1 is treated once with power 300 Watt.

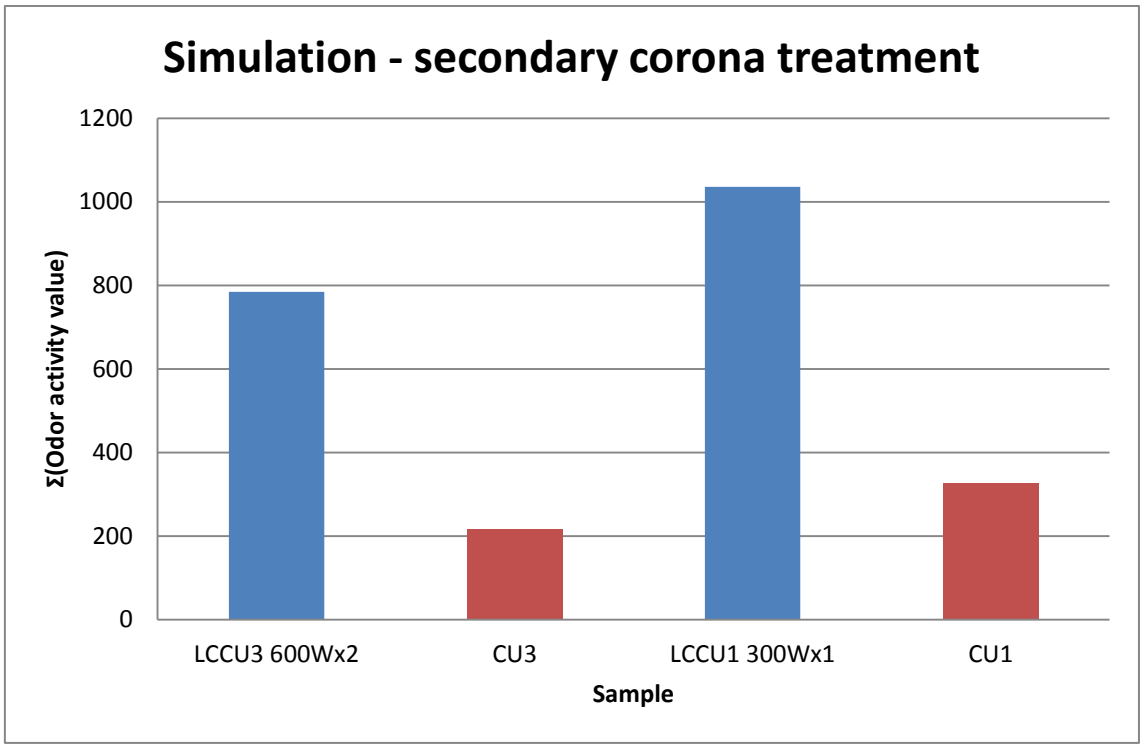


Figure 10.2: Simulation of secondary corona treatment

The third example of the modified samples is coated paperboard which was treated by the corona one additional time. This process does not take place in industry and could be called “tertiary corona treatment”. This data shows that a surplus of the corona can lead to a decrease of the overall odor activity value.

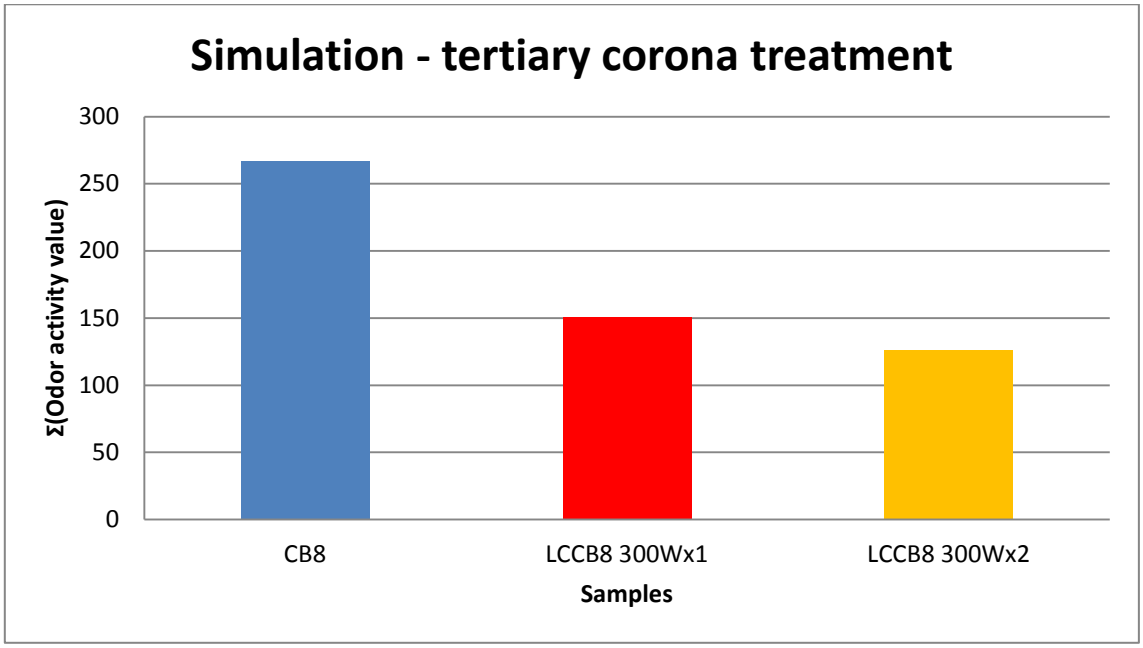


Figure 10.3: Simulation of the “tertiary” corona treatment

10.2 Results – Polyethylene

All three granulates show high overall odor activity values (up to 500) which are not typical for either uncoated nor for coated paperboard. Each granulate has two odor activity values, one at 200 °C and another at 215°C. The odor activity values seem to be influenced by the temperature change. The OAVs are on average 45 % lower at 200 °C compared to the OAVs at 215 °C.

Aldehydes considered in this calculation were saturated C6-C10 aldehydes. Of course there are more aldehydes that are formed through polyethylene oxidation. It can be assumed that not all of them are stable and therefore are found only in the finished product.

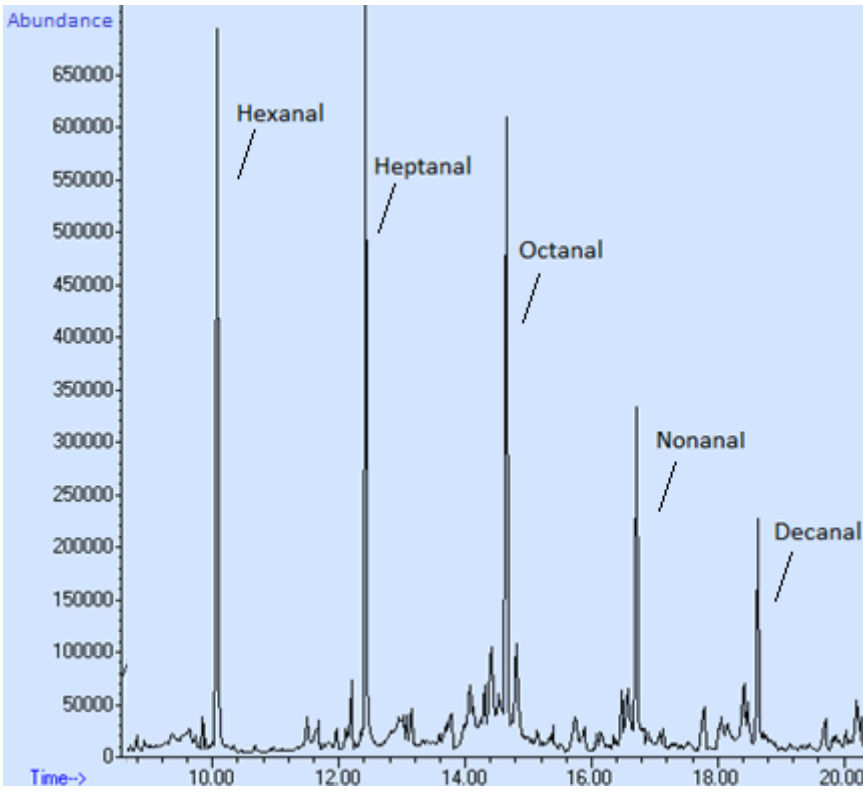


Figure 10.4: Granulate 1 (Ion 44 m/z extracted in SIM Modus), formed aldehydes during the thermal treatment of the polyethylene at 200 °C.

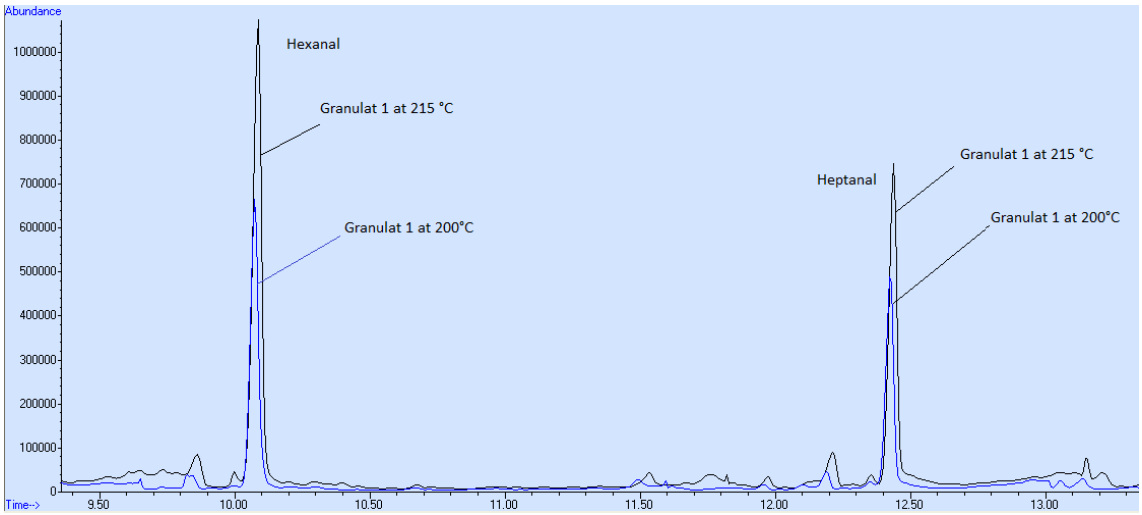


Figure 10.5: Granulate 1 (Ion 44 m/z extracted in SIM Modus), temperature influence on the hexanal and heptanal formation during the thermal treatment of the polyethylene.

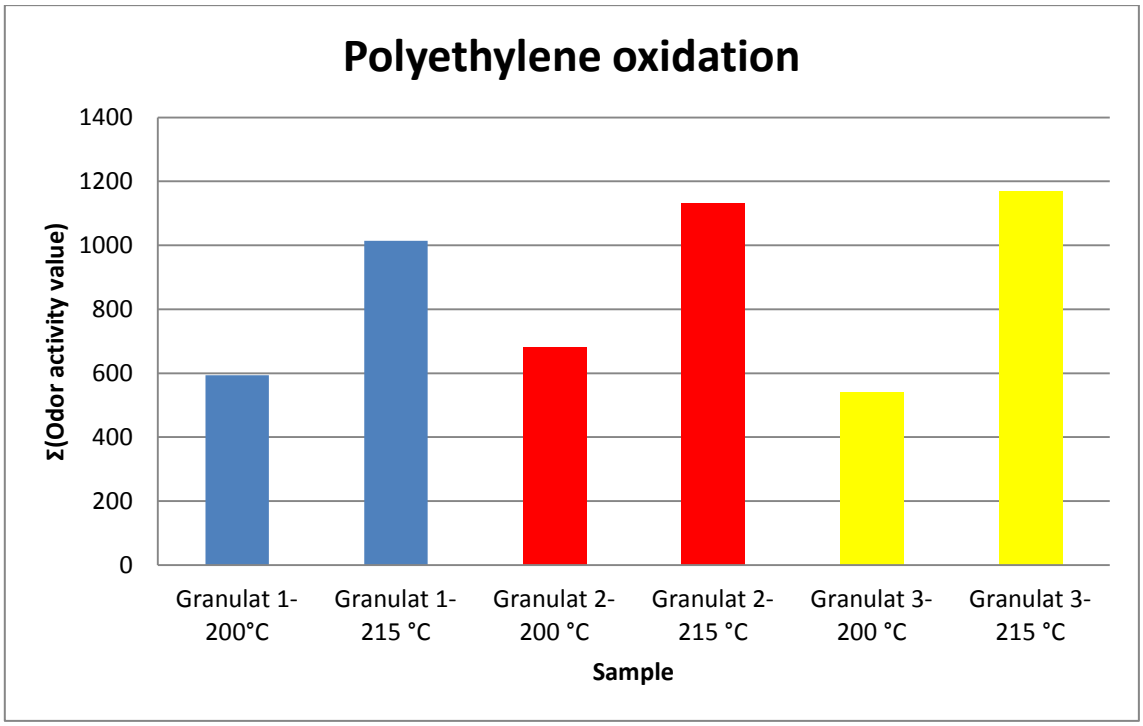


Figure 10.6: Influence of temperature on polyethylene odor activity value

11. Sensorial Analysis

All samples had an overall grade for odor intensity above 2 with just three exceptions. (Sample CU4- 1,5). The odor descriptions make it apparent that all of the analyzed samples have an aldehydic odor or mixture of the different odors which indicate that aldehydes are the main odorants.

Table 11.1: Odor grades of uncoated (UB), coated (CB) and coated-corona untreated (CU) paperboard

Sample	Odor intensity	Odor description
UB1	2	Cardboard, fatty, sweet
CU1	3	Green-grass, cucumber, aldehydic –C6, rancid
CB1	3	Green-grass, fatty, oil cucumber, aldehydic –C6, rancid
UB2	2	Muggy, light fatty, varnish
CU2	2	Spicy, rancid, fatty, cardboard
CB2	3	Fatty, light rancid, aldehydic, green
UB3	2,5	Glue, cardboard, aldehydic, fatty, sweet
CU3	2	Glue,aldehydic,fatty,sweet
CB3	2	Cardboard,pungent,lack,light plastic
UB4	2	Green, aldehydic, rancid, fatty, sweetly, oil
CU4	1,5	Fatty, light rancid, aldehydic, green
CB4	2,5	pungent, fatty, cardboard, rancid
CB6	3	Fatty, sweet, aldehydic
UB6	3	Dusty, cardboard, light fatty-sweet
CB7	2,8	Aldehydic, fatty, green, cucumber
UB7	3	Fatty, aldehydic, plastic
UB8	2,5	Cardboard, paper, without plastic smell,
CB8	3	Resin smell, aldehydic, plastic, intensive aldehydic
UB9	3	Fatty, rancid, phenolic, smell, aldehydic, cardboard,
CB9	2	Dusty, oxidized polyethylene smell, fatty, varnish, aldehydic

The coated paperboard showed an overall average intensity of 2.7 compared with uncoated paperboard which has a slightly lower average intensity 2.5. Coated paperboard-corona untreated has an average of 1.8. The coated paperboard has

polyethylene as second source of the odor. The coated paperboard, which is corona untreated has lower intensity because of the fact that corona untreated samples are less oxidized. The results cannot be compared with instrumental methods because of the fact that sensorial analysis and instrumental analysis were not performed at the same time; the sensorial analysis could be seen as a supplement to the qualitative analysis. It confirms the qualitative instrumental analysis, where it has been found that the odor comes from aldehyde.

In the figure 11.1 is shown that time has an influence on the oxidation process of the linoleic acid. The oxidation process is accelerated at higher temperatures and therefore, reaches the saturation point earlier, even at 20 °C and sufficient time, the oxidation process proceeds.

Furthermore, the direct correlation between sensorial and instrumental data can not be established.

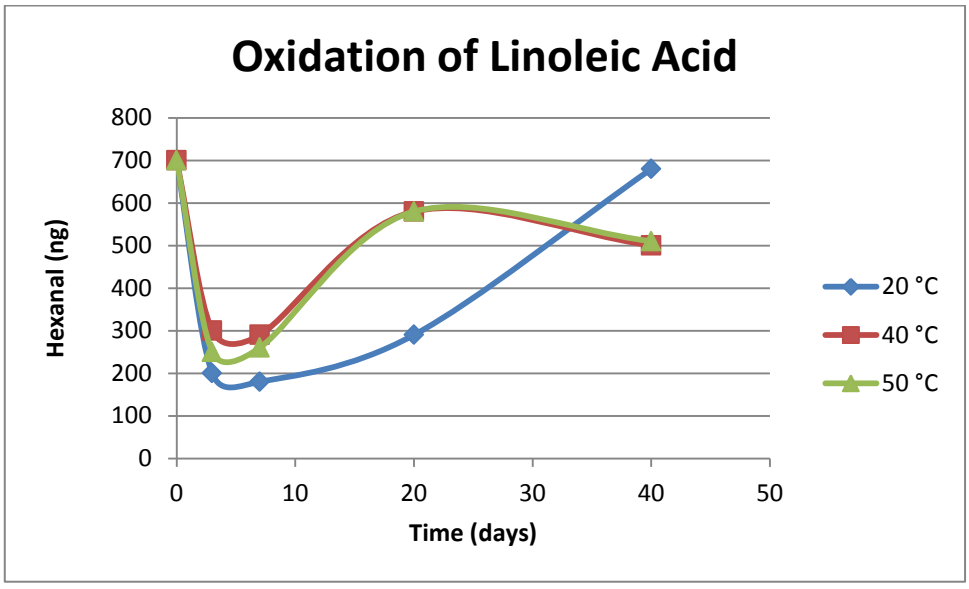


Figure 11.1: The sample of 1 g paperboard has been impregnated with 10 mg linoleic acid and stored for 42 days at different temperature and measured by the GC-MC. [8]

12. Conclusion

There are many logical trends which could be explained by present theories. However some results are hard to explain because of the insufficient data, measurements, and lack of work done in this field.

Odor was caused by the aldehydes for all samples as indicated from instrumental as well as sensorial analysis. The odors are descriptions clearly indicate the presence of the aldehydes in the samples being analyzed.

The pulp has lower odor activity values than other samples. Theoretically, other odor active compounds besides aldehydes could also be found in those samples. Aldehydes are a dominant product of the oxidation of the linolenic acid and linoleic acid, which are natural components of the pulp.

The figures showed it is clear that uncoated paperboard has lower odor activity values than those from coated paperboard. The uncoated paperboard has a slightly lower intensity value from the sensorial analysis. The main source for the odorants in the paperboard come from natural pulp components, but unfortunately the pulp odor quality is not stable and therefore it is not possible to correlate those two sample categories.

The coated paperboard is the finished product and it has higher amounts of odorants than other samples. The contribution of the polyethylene to the odor development is very significant and could be seen from these experiments.

Small temperature differences on the extrusion process could have relevant consequences for the off-odor of the product. This could be a future topic for the optimization of the coating plant.

The process site the corona treatment has two effects on the paperboard. The oxidation process secures the formation of organic compounds on the sample surface. The corona process in terms of paperboard coating is not a well explored process. In literature there are many studies with regards to the effect of the corona treatment, but in different contexts. The formation of ozone could be one reason for the decomposition of the odor active compounds formed on the surface. Unfortunately the experiments with the corona

are just case studies and could also be considered as an interesting area for further investigation.

The results also indicate that the corona is a very promising field when it comes to odor development studies.

All of the samples which are coated have different grammage and coating amounts of polyethylene. The different trends in odor development should be taken as normal, because of the fact that the different amount of the substrate is exposed to the same corona treatment or same process parameters.

The example which has a grammage of 40 g/m² and is coated with 20 g of polyethylene per square meter from the chemical point of view cannot behave the same as the sample which has a grammage of 280 g/m² and it is coated with 20 g of polyethylene. The first sample has a mass fraction of 33 % LDPE and second 6.6 % LDPE. If the polyethylene is seen as a substrate for the formation of the aldehydes, the first sample under the same process parameter will have a higher amount of odorants than the second sample.

Future studies of the odor development through the optimization of the key process units such as corona treatment, and optimization of the process parameters such as temperature, have great potential. Regarding paper production, quality control over raw materials is a necessity in order to control odor development. The finished product must also be controlled by the sensorial analysis in order to avoid consumer complaints.

Bibliography

[1] Young Teck Kim, Byungjin Min, and Kyung Won Kim, *Innovations in Food Packaging, Chapter 2,General Characteristics of Packaging Materials for Food Systems,* Second edition,2014.

[2] G. Ziegleder,"*Volatile and Odorous Compounds in Unprinted Paperboard*", Packag. Technol. Sci.11, 231-239, 1998.

[3] Thomas Robert Wenzl, *"Systematische Untersuchung der Dampfphasenverteilungsgleichgewichte und der Dampfphasenextraktion von sensorisch aktiven Substanzen aus Verpackungsmaterialien"*, Dissertationsarbeit TU Graz, 2-7; 9-25, 1996-2000.

[4] Knut Wiik and Torbjørn Helle, *"Problems with paper odor and possible ways to solve them"*, Trondheim University of Technology, 2012.

[5] Anja Veijanen, *"A integrated sensory and analytical method for identification of off-flavor compounds"*, Research report no. 34, Finland, 27-29; 37-38, 1990.

[6] Erwin Polmann, Corina Schmidt and Bryant McEwen, *PTS Magazine for paper industry 02/10, English edition*, Verlag Papiertechnische Stiftung (PTS), Germany, 11-14, 2010.

[7] Ben Nijssen, Tno-Civo*, "Off-Flavors",* Food Analysis Institute, Zeist, Netherlands, 689-692, 2011.

[8] S. Pugh and J.T. Guthrie, *"Development of taint and odour in cellulosic carton-board packaging systems"*, Kluwer Academic Publishers, 247–262, 2000.

[9] Helene Hopfer,Nina Haar,Wolfgang Stockreiter,Christian Sauer,Erich Leitner, "Combining different analytical approaches to identify odor formation mechanisms in polyethylene and polypropylene", Springer-Verlag 2012, 2012.

[10] Knut Wiik, Marit Gromsrud, Torbjørn Helle, "*Studies on odour reduction in TCF bleached packaging paper"*, Norwegian University of Science and Technology, Norway, 2014.

[11] Steffen Strassnig, *"Flüchtige Lipidoxidationsprodukte on Celluloseprodukten und biologischene Materialien"*, Dissertationsarbeit TU Graz, 15-25, 1997-2002.

[12] Rene Eckhart, Virgin fiber, TU Graz, Chapter 4, 35-37, 2012.

[13] Jurkka Kuusipalo, *"Paper Converting Technology, Paper and Paperboard Converting"* Publisher: Finnish Paper Engineers' Association,108-145.

[14]http://www.ahlbrandt.de/index.php?page=corona-behandlung-2, 12.10.2014.

[15] Thermo Fischer Scientific, Unit Lab Services Training Courses, European Training Institute, ISQ Operations Manual, 7-50, 2014.

[16] Thorbjörn Andersson, Bengt Wesslen, John Sandström, *"Degradation of Low Density Polyethylene during Extrusion. I. Volatile Compounds in Smoke from Extruded"* Films,Wiley, Sweden, 1584-1586,2012.

[17] Thorbjörn Andersson, Bengt Wesslen, John Sandström*, "Degradation of Low Density Polyethylene During Extrusion. III. Volatile Compounds in Extruded Films Creating Off-Flavor"*, Sweden, Wiley, 848-858, 2004.

[18] Thorbjörn Andersson,Max Hallin Holmgren,Tim Nielsen,Bengt Wessle´n, *"Degradation of Low Density Polyethylene During Extrusion. IV. Off-Flavor Compounds in Extruded Films of Stabilized LDPE"*, Wiley, Sweden, 584-594, 2004.

[19] Odor activity value definition, http://www.chromedia.org/chromedia, 07.01.2015

[20] Knut Wiik and Torbjörn Helle, *"Mechanisms of paper odor release"*, Norway, 268-270, 1999.

[21] Odor threshold concentration definition, http://www.safeopedia.com/definition/dor, 14.01.2014.

[22] Shimadzu Comprehensive GCxGC System, http://www.shimadzu.com, 09.01.2015.

[23] Dian Fedl, "*Application of Multidimensional Gas Chromatography to the Analysis of Odor-active Compounds"*, Graz, 5-18, 2012.

[24] R. Schnick, Korona-Vorbehandlung, ITW Surface Treatment, Germany, 1-7, 2008.

[25] Tadeusz Gorecki, James Harynuk and Ognjen Panic,"*Comprenhensive two-dimensional gas chromatography (GCxGC)"*, Chapter 6, Department of Chemistry,. University of Waterloo, Canada, 65-73, 2010.

[26] George Wypych, *Handbook of Odors in Plastic Materials, ChemTec Publishing*,Toronto, 148-160, 2013.

[27]http://www.analytik.ethz.ch/vorlesungen/biopharm/Trennmethoden/AnalytischeChemie_Skript_4_GC.pdf 93-116, 2015.

[28] Leo M.L. Nollet, Fidel Toldra, *"Sensory Analysis of Foods of Animal Origin"*, CRC Press USA, 403-405, 2010.

[29] www.d.umn.edu,*"Quantitative Gas Chromatography",* Chem 2223 Lab Prep, 1-10.

[30] Paula Vera,Blanca Uliaquea,Elena Canellas,Ana Escudero,Cristina Nerína, *"Identification and quantification of odorous compounds from adhesives used in food packaging materials by headspace solid phase extraction and headspace solid phase microextraction coupled to gas chromatography–olfactometry–mass spectrometry"*, Analytica Chimica Acta 745 (2012), 53– 63, 2012.

[31] Henryk H. Jele´ n, Małgorzata Majchera, Mariusz Dziadasa, "*Microextraction techniques in the analysis of food flavor compounds"*, Analytica Chimica Acta, 2012.

[32] Johanna Lahti, *Corona (discharge) treatment*, Tampere University of Technology, 1-13, 2012.

[33] ÖNORM EN 1230·1, *Papier und Pappe vorgesehen für den Kontakt mit Lebensmitteln-Sensorische Analyse*, Teil 1: Geruch, Ausgabe 2010.

[34] Manfred Rothe, *Handbook of Aroma Research*, Kluwer Academic, USA , 1998.

[35] Gottfried Ziegleder, Brigitte Stumpf, Eva Stojacic, „*Nachweis oxidativer Fehlgerüche in unbedrucktem Karton-Beitrag zur Qualitätskontrolle von Lebensmittelverpackungen"*, Nr.3, LVT Lebensmittel-Industrie 42, 143-150, 1997

[36] http://www.cyclochem.com/cyclochembio/research_e/039.html,January 2015.

[37] Jürgen Blechschmidt, *Taschenbuch der Papiertechnik Taschenbuch*, Carl Hanser Verlag GmbH & Co., 142-151,216-243, 2010.

[38] http://www.chemteam.info/Matter/PhysicalChemProperties.html, January 2015.

[39] Thorbjörn Andersson and Bengt Wesslén, *Degradation Of LDPE LLDPE and HDPE In Film Extrusion*, Lund Sweden, 2014.

[40] W. Grosch, *Aromastoffe aus der Lipidperoxidation*, Fat Sci. Technology, Nr.1, 1989.

[41] Gangfeng Ouyang, *Handbook of Solid Phase Microextraction, SPME and Environmental Analysis*, 2012.

[42] www.as.nchu.edu.tw/labf/aroma, 314-345, January 2015.

Appendix: Samples Tables and Calibrations Curve

A.1 Polyethylene Samples

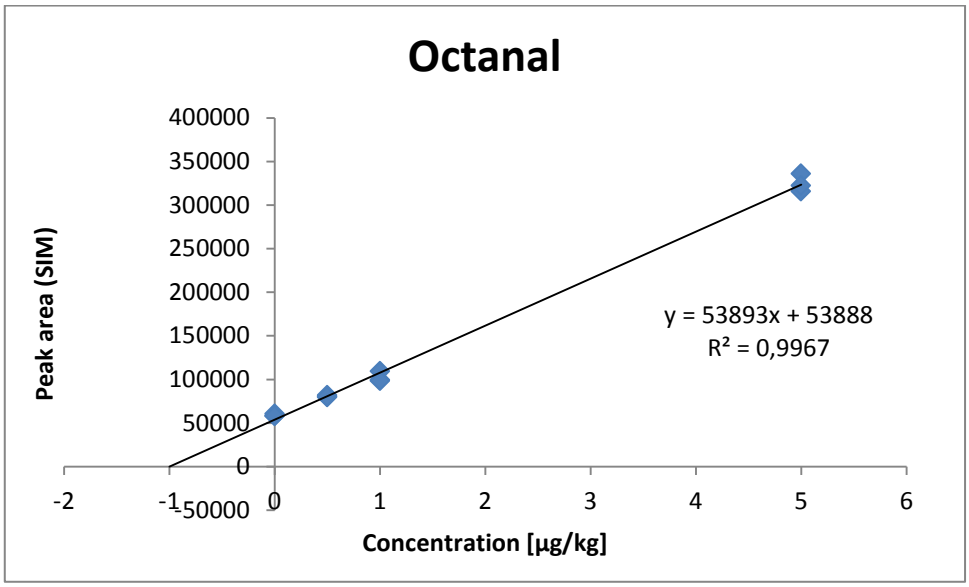
Table 1.1: Polyethylene- odor activity values

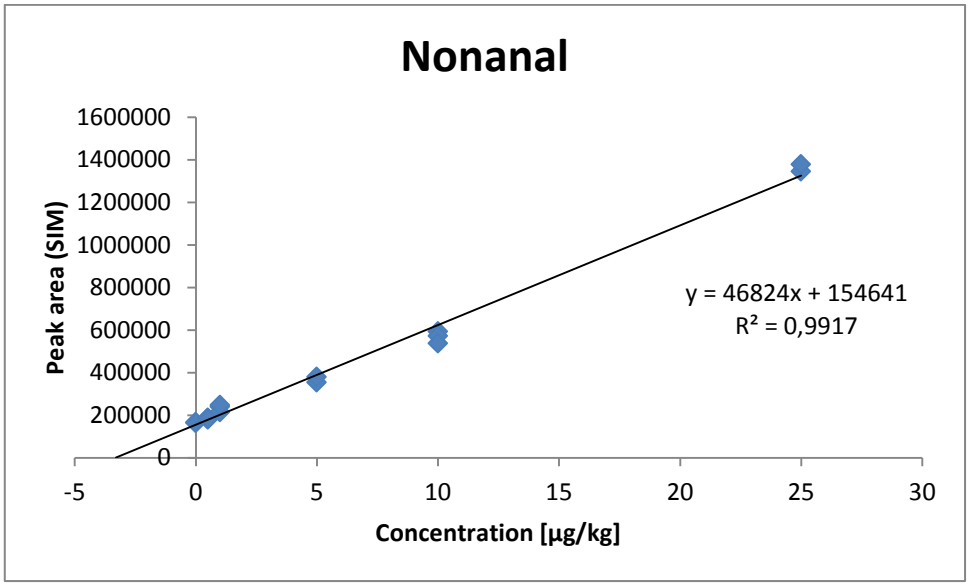
Sample:	Granulate 1-200°C	Granulate 1-215 °C	Granulate 2- 200 °C	Granulate 2-215 °C	Granulate 3-200 °C	Granulate 3- 215 °C
$OAV_{analyte}$						
Hexanal	72.7	153.4	78.6	92.3	63.0	122.5
Heptanal	56.1	125.2	80.4	89.5	67.6	107.8
Octanal	72.3	22.3	9.8	7.0	91.0	158.9
Nonanal	143.3	61.7	169.5	354.8	140.9	196.0
Decanal	248.4	651.2	342.6	588.5	175.5	583.6
∑ OAV	593	1014	681	1132	538	1169

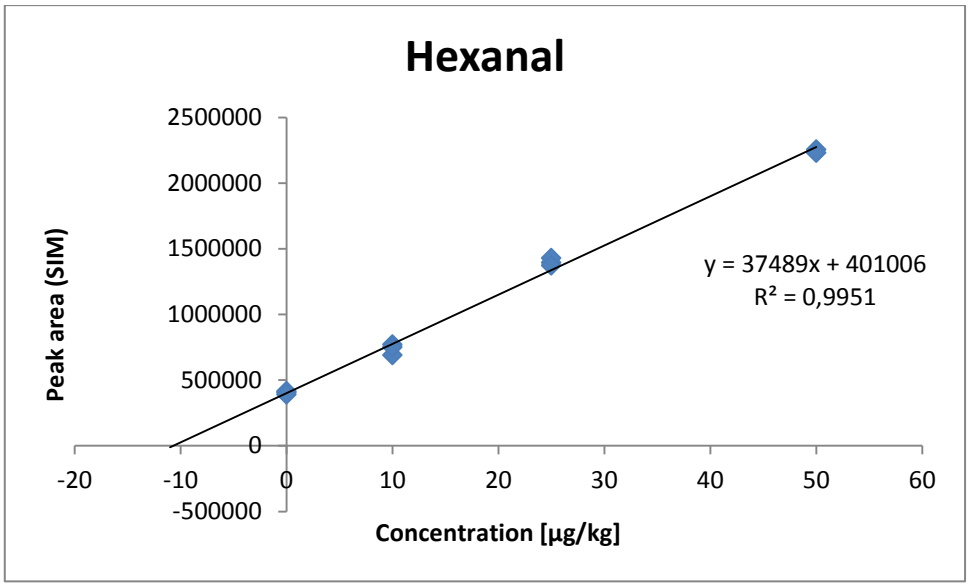
Table 1.2: Polyethylene- analyte

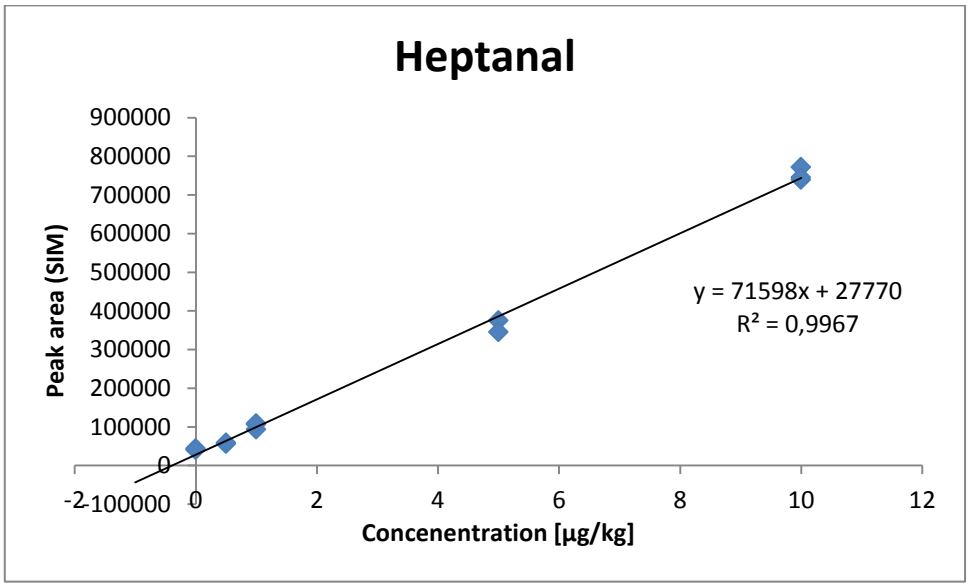
Sample:	Granulate 1-200°C [µg/kg]	Granulate 1-215 °C [µg/kg]	Granulate 2- 200 °C [µg/kg]	Granulate 2-215 °C [µg/kg]	Granulate 3-200 °C [µg/kg]	Granulate 3- 215 °C [µg/kg]
Analyte						
Hexanal	5449	11507	5895	6921	4727	9184
Heptanal	1570	3505	2250	2507	1892	3017
Octanal	1519	469	206	147	1910	3337
Nonanal	2724	1172	3220	6741	2677	3724
Decanal	5215	13676	7194	12358	3685	12256

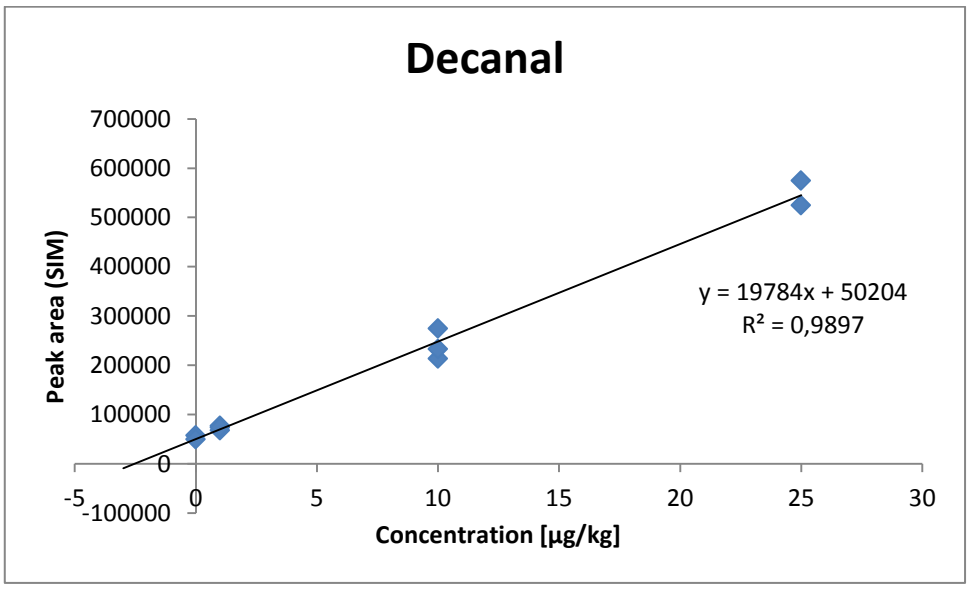
A.2 Calibrations Curve- Standard addition

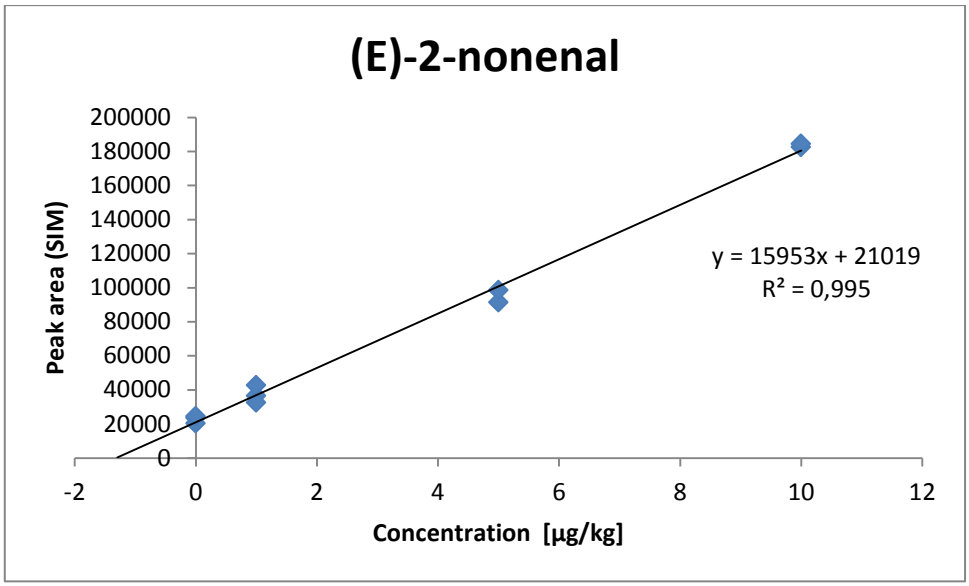





Hexanal
2500000
2000000
1500000
1000000
500000
0
-500000
-20
-10
0
10
20
30
40
50
60
Peak area (SIM)
Concentration [µg/kg]
y = 37489x + 401006
R² = 0,9951


Heptanal
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
-2
0
2
4
6
8
10
12
Peak area (SIM)
Concenentration [µg/kg]
y = 71598x + 27770
R² = 0,9967


Decanal
700000
600000
500000
400000
300000
200000
100000
0
-100000
-5
0
5
10
15
20
25
30
Peak area (SIM)
Concentration [µg/kg]
y = 19784x + 50204
R² = 0,9897


(E)-2-nonenal
Peak area (SIM)
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-2
0
2
4
6
8
10
12
Concentration [µg/kg]
y = 15953x + 21019
R² = 0,995

A3.1 Pulp Samples

Sample PA1		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	94.9	1.3
Heptanal	3.6	0.1
Octanal	6.0	0.3
Nonanal	34.1	1.8
Decanal	19.5	0.9
(E)-2-Nonenal	6.4	32.1
∑ OAV		36

Sample PA2		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	110.1	1.5
Heptanal	2.3	0.1
Octanal	2.9	0.1
Nonanal	10.8	0.6
Decanal	12.2	0.6
(E)-2-Nonenal	2.2	11.0
∑ OAV		14

Sample PB1		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	11.1	0.1
Heptanal	1.4	0.1
Octanal	2.2	0.1
Nonanal	23.3	1.2
Decanal	17.4	0.8
(E)-2-Nonenal	3.0	15.2
∑ OAV		18

Sample PB2		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	12.3	0.2
Heptanal	1.3	0.0
Octanal	2.1	0.1
Nonanal	21.7	1.1
Decanal	11.6	0.6
(E)-2-Nonenal	2.9	14.3
∑ OAV		16

Sample PC1		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	7.5	0.1
Heptanal	1.6	0.1
Octanal	2.8	0.1
Nonanal	16.8	0.9
Decanal	15.7	0.7
(E)-2-Nonenal	4.6	22.9
∑ OAV		25

Sample PC2		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	32.1	0.4
Heptanal	1.5	0.1
Octanal	2.2	0.1
Nonanal	9.3	0.5
Decanal	11.7	0.6
(E)-2-Nonenal	2.3	11.6
∑ OAV		14

Sample PD3		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	22.4	0.3
Heptanal	1.2	0.0
Octanal	2.1	0.1
Nonanal	9.8	0.5
Decanal	9.8	0.5
(E)-2-Nonenal	1.5	7.7
∑ OAV		9

Sample PD2		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	24.7	0.3
Heptanal	1.4	0.1
Octanal	1.9	0.1
Nonanal	10.4	0.5
Decanal	13.7	0.7
(E)-2-Nonenal	1.5	7.7
∑ OAV		9

Sample PC3		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	5.1	0.1
Heptanal	0.7	0.0
Octanal	2.3	0.1
Nonanal	8.9	0.5
Decanal	10.5	0.5
(E)-2-Nonenal	3.3	16.3
∑ OAV		17

Sample PD1		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	32.1	0.4
Heptanal	1.5	0.1
Octanal	2.2	0.1
Nonanal	9.3	0.5
Decanal	11.7	0.6
(E)-2-Nonenal	2.3	11.6
∑ OAV		14

Sample PB3		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	7.6	0.1
Heptanal	1.1	0.0
Octanal	2.3	0.1
Nonanal	23.9	1.3
Decanal	13.4	0.6
(E)-2-Nonenal	1.2	6.1
∑ OAV		8

A.3.2 Paperboard Samples

Sample CB1		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	498.4	6.6
Heptanal	26.8	1.0
Octanal	17.8	0.8
Nonanal	342.7	18.0
Decanal	73.2	3.5
(E)-2-Nonenal	52.2	261.0
∑ OAV		291

Sample CU1		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	470.3	6.3
Heptanal	29.2	1.0
Octanal	21.9	1.0
Nonanal	442.0	23.3
Decanal	89.7	4.3
(E)-2-Nonenal	58.1	290.5
∑ OAV		326

Sample UB1		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	190.0	2.5
Heptanal	6.6	0.2
Octanal	6.3	0.3
Nonanal	48.9	2.6
Decanal	19.4	0.9
(E)-2-Nonenal	23.9	119.4
∑ OAV		116

Sample CB5		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	410.3	5.5
Heptanal	32.0	1.1
Octanal	14.0	0.7
Nonanal	444.0	23.4
Decanal	79.7	3.8
(E)-2-Nonenal	56.2	281.0
∑ OAV		315

Sample CU5		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	276.8	3.7
Heptanal	11.9	0.4
Octanal	13.6	0.6
Nonanal	125.8	6.6
Decanal	58.5	2.8
(E)-2-Nonenal	89.6	448.0
∑ OAV		462

Sample UB5		**1.0**
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	32.3	0.4
Heptanal	2.1	0.1
Octanal	3.2	0.2
Nonanal	14.0	0.7
Decanal	9.3	0.4
(E)-2-Nonenal	3.4	17.2
∑ OAV		19

Sample CB6		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	191.2	2.5
Heptanal	15.9	0.6
Octanal	15.9	0.8
Nonanal	313.4	16.5
Decanal	68.8	3.3
(E)-2-Nonenal	55.0	275.0
∑ OAV		299

Sample CU6		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	402.5	5.4
Heptanal	24.2	0.9
Octanal	6.2	0.3
Nonanal	436.2	23.0
Decanal	71.9	3.4
(E)-2-Nonenal	77.2	386.0
∑ OAV		419

Sample UB6		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	32.0	1.5
Heptanal	2.2	0.3
Octanal	3.2	0.5
Nonanal	20.5	9.2
Decanal	10.6	2.0
(E)-2-Nonenal	29.5	161.0
∑ OAV		174

Sample UB2		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	133.9	1.8
Heptanal	12.4	0.4
Octanal	15.6	0.7
Nonanal	46.3	2.4
Decanal	15.5	0.7
(E)-2-Nonenal	4.2	21.0
∑ OAV		27

Sample CB2		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	118.2	1.6
Heptanal	9.1	0.3
Octanal	11.8	0.6
Nonanal	236.8	12.5
Decanal	73.5	3.5
(E)-2-Nonenal	35.8	178.9
∑ OAV		197

Sample CU2		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	103.3	5.2
Heptanal	11.5	6.1
Octanal	18.8	120.5
Nonanal	371.4	47.0
Decanal	111.7	20.5
(E)-2-Nonenal	36.4	175.3
∑ OAV		209

Sample CB3		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	189.5	2.5
Heptanal	7.7	0.3
Octanal	9.5	0.5
Nonanal	144.5	7.6
Decanal	70.0	3.3
(E)-2-Nonenal	21.7	108.3
∑ OAV		123

Sample CU3		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	273.5	3.6
Heptanal	11.9	0.4
Octanal	13.9	0.7
Nonanal	210.1	11.1
Decanal	53.7	2.6
(E)-2-Nonenal	39.7	198.6
∑ OAV		217

Sample UB3		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	232.5	3.2
Heptanal	6.3	0.2
Octanal	6.7	0.3
Nonanal	46.2	2.9
Decanal	19.7	1.1
(E)-2-Nonenal	18.9	92.3
∑ OAV		100

Sample CB8		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	331.5	4.4
Heptanal	21.7	0.8
Octanal	19.5	0.9
Nonanal	260.5	13.7
Decanal	57.8	2.8
(E)-2-Nonenal	48.9	244.5
∑ OAV		267

Sample UB8		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	277.9	3.7
Heptanal	8.5	0.3
Octanal	6.1	0.3
Nonanal	22.8	1.2
Decanal	18.9	0.9
(E)-2-Nonenal	13.0	65.0
∑ OAV		71

Sample CB4		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	103.8	1.4
Heptanal	6.5	0.2
Octanal	7.8	0.4
Nonanal	65.8	3.5
Decanal	34.4	1.6
(E)-2-Nonenal	36.0	180.0
∑ OAV		187

Sample UB4		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	46.1	0.6
Heptanal	4.3	0.2
Octanal	5.6	0.3
Nonanal	26.1	1.4
Decanal	13.5	0.6
(E)-2-Nonenal	11.1	55.5
∑ OAV		59

Sample CU4		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	139.6	1.9
Heptanal	8.4	0.3
Octanal	9.1	0.4
Nonanal	95.2	5.0
Decanal	38.1	1.8
(E)-2-Nonenal	40.2	201.0
∑ OAV		210

Sample CB10		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	355.0	4.7
Heptanal	32.4	1.2
Octanal	28.0	1.3
Nonanal	356.9	18.8
Decanal	62.6	3.0
(E)-2-Nonenal	92.8	463.8
∑ OAV		493

Sample UB10		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	190.1	2.5
Heptanal	8.5	0.3
Octanal	6.7	0.3
Nonanal	20.3	1.1
Decanal	15.8	0.8
(E)-2-Nonenal	5.6	28.2
∑ OAV		33

Sample UB13		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	26.4	0.4
Heptanal	2.0	0.1
Octanal	2.9	0.1
Nonanal	18.9	1.0
Decanal	12.9	0.6
(E)-2-Nonenal	4.4	22.0
∑ OAV		24

Sample CB13		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	360.1	4.8
Heptanal	0.4	0.0
Octanal	18.6	0.9
Nonanal	141.2	7.4
Decanal	35.3	1.7
(E)-2-Nonenal	60.6	302.8
∑ OAV		318

Sample UB12		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	102.8	1.4
Heptanal	6.1	0.2
Octanal	9.2	0.4
Nonanal	131.2	6.9
Decanal	82.5	3.9
(E)-2-Nonenal	5.0	24.9
∑ OAV		38

Sample CB12		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	528.1	7.0
Heptanal	36.6	1.3
Octanal	30.8	1.5
Nonanal	478.3	25.2
Decanal	60.4	2.9
(E)-2-Nonenal	55.2	276.2
∑ OAV		314

Sample CB7		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	232.0	3.1
Heptanal	12.0	0.4
Octanal	13.0	0.6
Nonanal	200.0	10.5
Decanal	56.0	2.7
(E)-2-Nonenal	48.8	244.0
∑ OAV		261

Sample CU7		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	186.0	2.5
Heptanal	8.9	0.3
Octanal	10.1	0.5
Nonanal	230.0	12.1
Decanal	54.7	2.6
(E)-2-Nonenal	53.7	268.5
∑ OAV		286.0

Sample UB7		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	145.0	1.9
Heptanal	7.0	0.3
Octanal	5.6	0.3
Nonanal	143.8	7.6
Decanal	34.0	1.6
(E)-2-Nonenal	17.9	89.5
∑ OAV		101

Sample CB9		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	191.2	2.5
Heptanal	14.9	0.5
Octanal	15.4	0.7
Nonanal	188.0	9.9
Decanal	53.7	2.6
(E)-2-Nonenal	21.5	107.5
∑ OAV		124

Sample UB9		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	78.0	1.0
Heptanal	3.4	0.1
Octanal	3.5	0.2
Nonanal	26.4	1.4
Decanal	15.4	0.7
(E)-2-Nonenal	17.0	85.0
∑ OAV		88

Sample UB11		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	122.3	1.6
Heptanal	9.9	0.4
Octanal	18.6	0.9
Nonanal	121.3	6.4
Decanal	117.2	5.6
(E)-2-Nonenal	13.8	69.0
∑ OAV		84

Sample CB11		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	344.0	4.6
Heptanal	2.0	0.1
Octanal	20.0	1.0
Nonanal	134.0	7.1
Decanal	32.0	1.5
(E)-2-Nonenal	55.0	275.0
∑ OAV		289

A3.3 Modified Paperboard Samples

Sample LCCB4 600Wx1		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	836.7	11.2
Heptanal	33.7	1.2
Octanal	47.9	2.3
Nonanal	496.4	26.1
Decanal	208.0	9.9
(E)-2-Nonenal	74.8	374.0
∑ OAV		425

Sample LCCB8 300Wx2		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	89.3	1.2
Heptanal	13.1	0.5
Octanal	21.0	1.0
Nonanal	349.8	18.4
Decanal	99.7	4.7
(E)-2-Nonenal	20.0	100.2
∑ OAV		126

Sample LCCB2 300Wx2		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	1508.9	20.1
Heptanal	55.0	2.0
Octanal	76.9	3.7
Nonanal	608.7	32.0
Decanal	269.1	12.8
(E)-2-Nonenal	77.9	389.7
∑ OAV		460

Sample LCCB2 300Wx1		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	1490.1	19.9
Heptanal	49.0	1.8
Octanal	57.3	2.7
Nonanal	661.9	34.8
Decanal	293.7	14.0
(E)-2-Nonenal	105.5	527.4
∑ OAV		601

Sample LCCB8 300Wx1		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	184.8	2.5
Heptanal	22.9	0.8
Octanal	34.6	1.6
Nonanal	515.5	27.1
Decanal	144.1	6.9
(E)-2-Nonenal	22.3	111.6
∑ OAV		151

Sample LCCU1 300Wx1		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	807.9	10.8
Heptanal	54.1	1.9
Octanal	87.7	4.2
Nonanal	1501.9	79.0
Decanal	457.0	21.8
(E)-2-Nonenal	183.7	918.3
∑ OAV		1036

Sample LCUB1 400Wx1		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	1189.2	15.9
Heptanal	41.8	1.5
Octanal	62.2	3.0
Nonanal	890.1	46.8
Decanal	398.7	19.0
(E)-2-Nonenal	86.9	434.6
∑ OAV		521

Sample LCUB2 400Wx2		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	679.3	9.1
Heptanal	19.6	0.7
Octanal	29.0	1.4
Nonanal	256.9	13.5
Decanal	141.2	6.7
(E)-2-Nonenal	68.3	341.7
∑ OAV		373

Sample LCUB4 400Wx1		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	865.1	11.5
Heptanal	29.9	1.1
Octanal	51.4	2.4
Nonanal	470.8	24.8
Decanal	246.5	11.7
(E)-2-Nonenal	57.6	288.1
∑ OAV		340

Sample LCCU3 600Wx2		
	Concentration [µg/kg]	Odor activity value (OAV)
Hexanal	568.2	7.6
Heptanal	66.6	2.4
Octanal	107.5	5.1
Nonanal	1537.2	80.9
Decanal	572.7	27.3
(E)-2-Nonenal	132.2	661.2
∑ OAV		784